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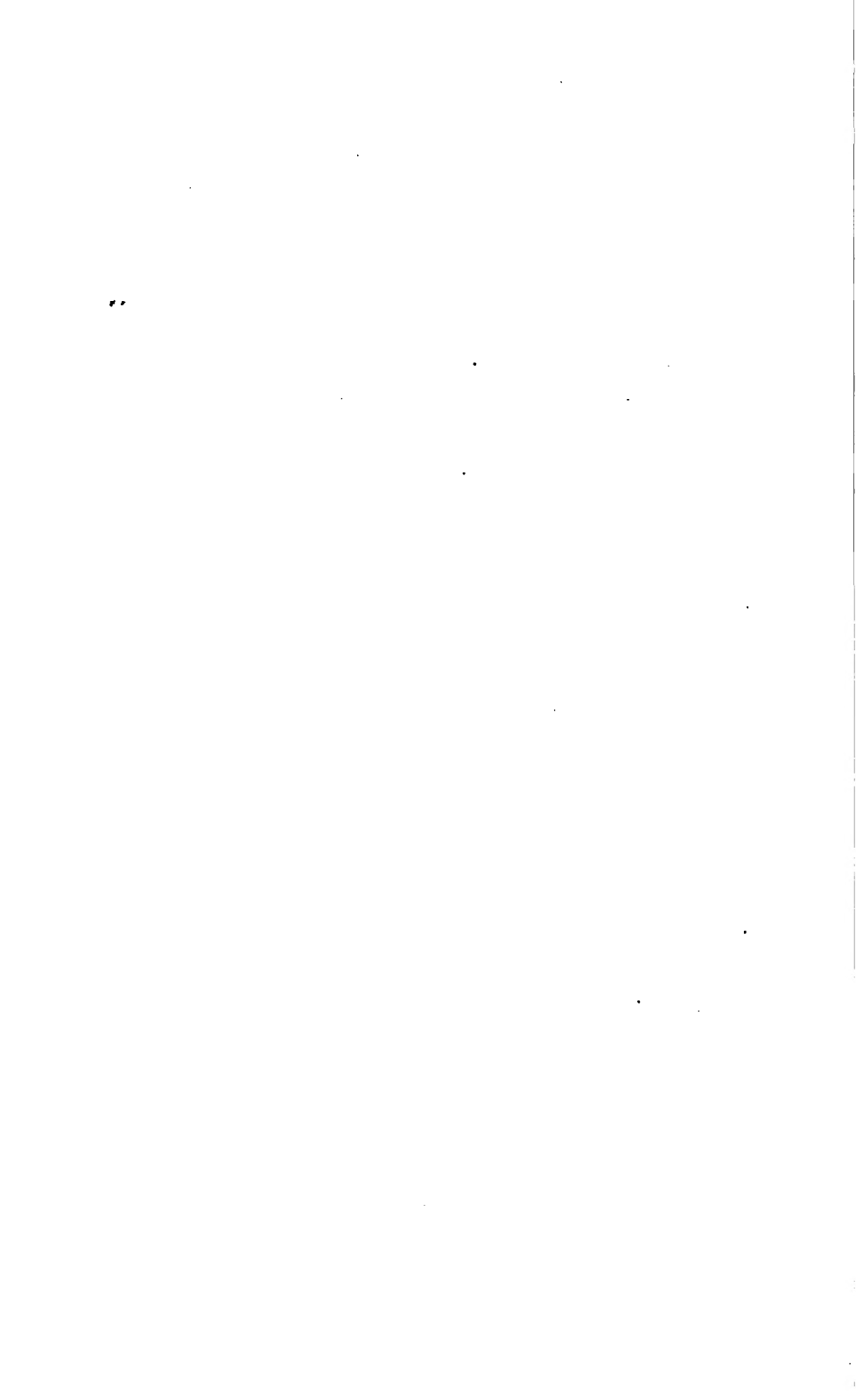
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A TREATISE  
ON THE  
PRINCIPLES OF CHEMISTRY.

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# A TREATISE

ON THE

## PRINCIPLES OF CHEMISTRY.



BY

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CAMBRIDGE.

"In nature everything is distinct, yet nothing defined into absolute  
independent singleness." WORDSWORTH.

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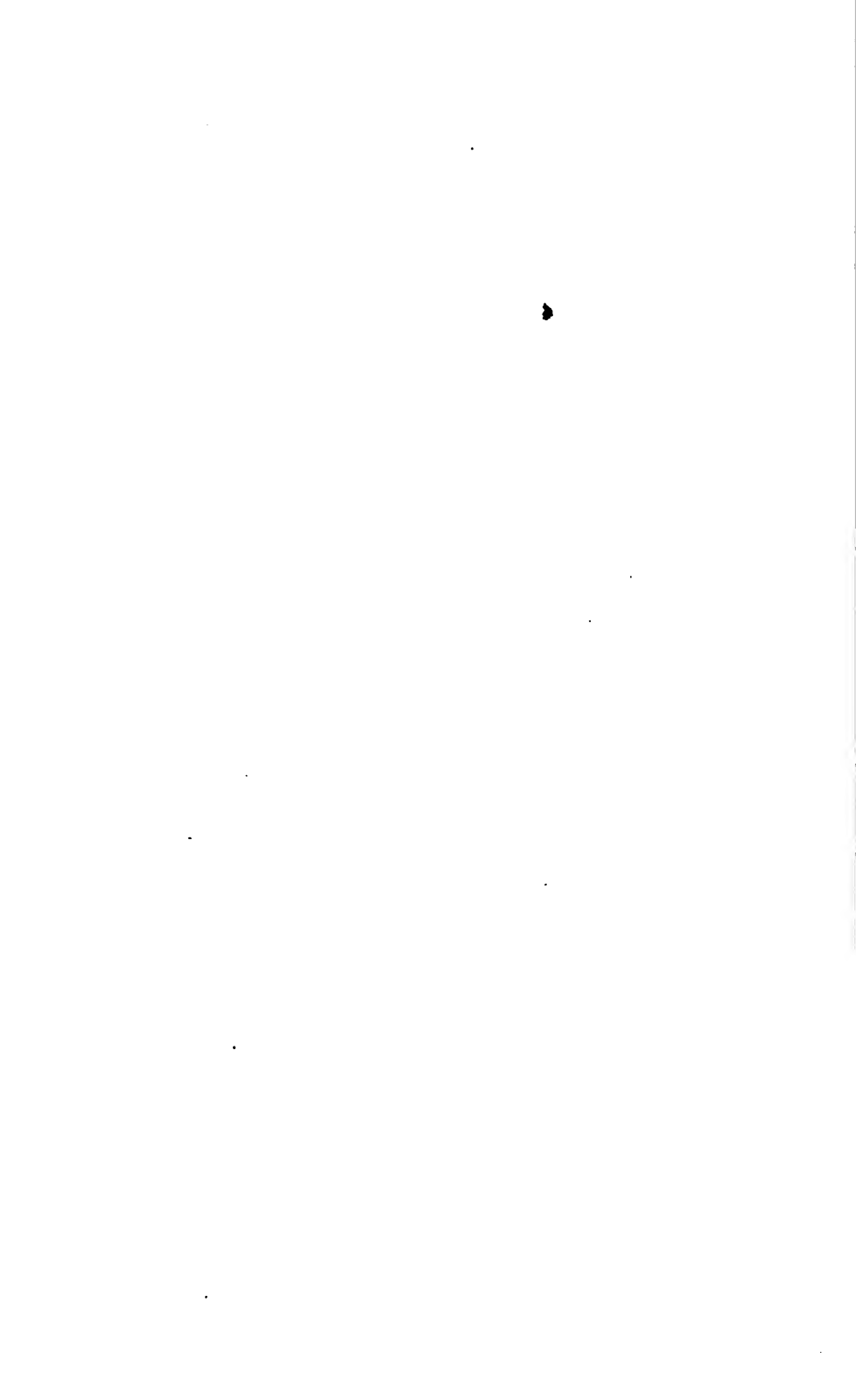
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*If in this book I have shewn any just  
appreciation of the scientific study of nature,  
I owe it to the teaching of*

PROFESSOR SIR WILLIAM THOMSON.

*To him, therefore, I dedicate my work.*





## PREFACE.

THIS book is intended to give a fairly complete account of the present state of knowledge regarding the principles and general laws of chemistry.

It is addressed to students of this science who have already a considerable acquaintance with descriptive chemistry, but it is hoped that by such students the book will be found complete in itself; so that while it certainly deals with chemical principles and theories on the supposition that its readers have some knowledge of chemical facts, yet the book may fairly claim to rank as a systematic treatise on chemical philosophy.

While I have tried to supply full information regarding those points which appear to me of most importance, I have also sought to avoid great detail, and to present a sketch of the principles of chemistry the parts of which shall hang together as being mutually dependent.

To know what to omit has been one of the most difficult parts of my undertaking. The chemical student is too often subjected to a shower-bath of facts; he is made to feel that

'to sit as a passive bucket and be pumped into...can in the long-run be exhilarating to no creature.'

An attempt is made in this book to treat the principal theories of modern chemistry to some extent from an historical point of view, and to trace the connections between the older theories and those which now prevail in the science. It is hoped that the student may thus gain a firmer grasp of those theories than he is able to do when they are put before him as entirely creations of recent times.

I have tried to deal with chemical facts and generalisations so as to shew their reality. This can best be done, I believe, by following in the very foot-prints of the great discoverers, by watching them as they make their footing sure, and as they feel their way up the heights. That the student may be able to verify the accounts I have given of the more important investigations, and more especially that he may fill in the details which I have necessarily omitted, I have given copious references to original memoirs and papers; these references will, I believe, be found correct, at least I have spared no pains to make them so. I have also endeavoured to make the index full and complete.

So far as I am aware, no sufficiently comprehensive guide to the study of the principles of chemistry exists, in an English form, although we have many excellent works dealing with descriptive chemistry, with the materials, that is to say, from which chemical science is being constructed. Professor Lothar Meyer's *Die Modernen Theorien der Chemie*, to a considerable extent meets the wants of the German student. I have made free use of that book in preparing my own; but I venture to think I have incorporated in my general plan many important facts and principles which do not find a

place in that admirable treatise. I have also regarded the whole subject from a stand-point somewhat different from that occupied by the German Professor.

To name all the books and journals from which I have derived assistance would be tedious and absurd; they are sufficiently indicated in the notes and references<sup>1</sup>.

I have tried to rest every important statement on first-hand authority. When chemistry is regarded from the point of view of the great workers therein, it wears an aspect very different from that with which it confronts the mere text-book-taster.

The book is divided into two parts. The first part is occupied with the statement and discussion of the atomic and molecular theory, and the applications thereof to such subjects as allotropy, isomerism, and the classification of elements and compounds. Somewhat full accounts are also given, in this part, of thermal, optical, and other departments of physical chemistry, in so far as the results and methods of these branches of the science are applicable to the questions regarding the composition of chemical systems which are connoted by the term Chemical Statics.

The second part of the book is devoted to the subjects of dissociation, chemical change and equilibrium, chemical affinity, and the relations between chemical action and the distribution of the energy of the changing system. These, and cognate questions, I have ventured to summarise in the expression Chemical Kinetics.

I have been much aided in my task by my friends Mr C. Slater, B.A., of St John's College, and Mr R. Threlfall,

<sup>1</sup> The full titles of the various journals referred to are given on pp. xxi, xxii.

B.A., Scholar of Gonville and Caius College. The former has read considerable portions of the proofs and has made many valuable suggestions ; the latter has read all, except the first chapter of Book I, and by his criticisms and remarks has helped me to make many important points much clearer and more accurate than they would otherwise have been.

M. M. PATTISON MUIR.

CAMBRIDGE, *October* 1884.

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# TITLES OF JOURNALS CONTAINING MEMOIRS TO WHICH REFERENCES ARE MADE.

## ABBREVIATED TITLES.

*Phil. Trans.*  
*Proc. R. S.*  
*C. S. Journal.*

*Phil. Mag.*  
*Chem. News.*  
*Nature.*  
*Brit. Ass. Reports.*

*Proc. R. I.*

*Amer. Chem. Journal.*  
 or { *Amer. Journ. of Sci. and Arts*  
       *Sill. Amer. Journal.* }

*Proc. Amer. Acad. of Arts and Sci.*  
*Gilbert's Ann.*

*Pogg. Ann.*

*Wied. Ann.*

*Pogg. Beiblätter.*

## FULL TITLES.

*Philosophical Transactions.*  
*Proceedings of the Royal Society.*  
*Journal of the Chemical Society.*  
 [Memoirs and Proceedings, 3 vols. (1841-1847).  
   Journal, **series 1**, 15 vols. (1848-1862).  
   ,, **series 2**, 15 vols. (1863-1877).  
   ,, **Transactions and Abstracts** paged separately, from 1878 to present time. The volumes of this Journal are sometimes referred to by numbers beginning with volume 1 of series 1, and running on consecutively to the present time.]

*Philosophical Magazine.* [**Series 1 to 5.**]  
*The Chemical News.* [Beginning from 1860.]  
*Nature.* [1879, and onwards.]  
*Reports of the British Association for the Advancement of Science.* [1831, and onwards.]  
*Proceedings of the Royal Institution of Great Britain.* [1851, and onwards.]  
*American Chemical Journal.* [1879, and onwards.]  
*American Journal of Science and Arts*; since 1880 the title is *American Journal of Science*. [Conducted by Sillimann, and subsequently by Sillimann and Dana. **Series 1 to 3.**]  
*Proceedings of the American Academy of Arts and Sciences.* [**Series 1 and 2.**]  
*Gilbert's Annalen der Physik und Chemie.* [1799-1824.]  
*Poggendorff's Annalen der Physik und Chemie.* [1824-1876.]  
*Wiedemann's Annalen der Physik und Chemie.* [Continuation of *Pogg. Ann.* from 1877; frequently quoted in memoirs, &c., as *Ann. Phys. Chem.* **Series 2.**]  
*Beiblätter zu den Annalen der Physik und Chemie.* [1877, onwards.]



ABBREVIATED TITLES.	FULL TITLES.
<i>Annalen.</i>	<i>Liebig's Annalen der Chemie und Pharmacie.</i> [Continued since Liebig's death under same title.]
<i>J. für prakt. Chemie.</i> <i>Ber.</i>	<i>Journal für praktische Chemie.</i> [Series 1 and 2.] <i>Berichte der Deutschen Chemischen Gesellschaft.</i> [Abstracts of papers published elsewhere are paged consecutively with the transactions until 1883; from 1884 and onwards the abstracts, <b>Referate</b> , are paged separately.]
OF { <i>Fresenius's Zeitschr.</i> } { <i>Zeitschr. anal. Chemie</i> } <i>Zeitschr. für Chemie.</i>	<i>Zeitschrift für analytische Chemie</i> , herausgegeben von Dr C. R. Fresenius. [1862, onwards.] <i>Zeitschrift für Chemie.</i> [Conducted by Beilstein and Fittig. Series 1 and 2. 1858 to 1871. Publication discontinued.]
<i>Zeitschr. für Krystallog.</i>	<i>Zeitschrift für Krystallographie und Mineralogie.</i> [1877, onwards.]
<i>Schweigger's Journal.</i>	<i>Journal für Chemie und Physik.</i> [Conducted by J. S. C. Schweigger. 1811-1833.]
<i>Sitzber. der K. Akad. zu Wien.</i>	<i>Sitzungsberichte der Mathematisch-naturwissen- schaftliche Classe der Kaiserliche Akademie der Wissenschaften (Wien).</i> [Each volume contains 2 or 3 parts ( <i>Abtheilungen</i> ); each part is bound and paged as a separate volume; the arrange- ment is perplexing.]
<i>Sitzber. der Wiss. Akad. zu Berlin.</i> <i>Jahresberichte.</i>	<i>Sitzungsberichte der Akademie der Wissenschaften zu Berlin.</i> [1854, and onwards.] <i>Jahresberichte über die Fortschritte der Chemie, &amp;c.</i> [Since 1873, Stædel has edited a very useful <i>Jahresber. über die Fortschritte auf dem Gebiete der Reinen Chemie.</i> ]
<i>Compt. rend.</i>	<i>Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.</i> [1835, onwards.]
<i>Mém. de l'Acad.</i>	<i>Mémoires de l'Académie Royale des Sciences de l'Institut de France.</i> [1816, onwards.]
<i>Ann. Chim. Phys.</i> <i>Bull. Soc. Chim.</i>	<i>Annales de Chimie et de Physique.</i> [Series 1 to 6.] <i>Bulletin de la Société Chimique de Paris.</i> [1864, onwards.]
<i>Mém. de la Soc. d'Arcueil.</i>	<i>Mémoires de Physique et de Chimie de la Société d'Arcueil.</i> [3 vols. 1807-1817.]
<i>Mém. couronn. de l'Acad. Brux.</i>	<i>Mémoires couronnés par l'Académie royale des Sciences et Belles-Lettres de Bruxelles.</i> [1827, onwards.]
<i>Ann. Min.</i>	<i>Annales des Mines.</i> [series 1 to 6.]

## CORRECTIONS AND ADDITIONS.

### PAGE

22. Bottom line ; *for* '186' *read* '18·6'.
38. Second line from top ; *for* 'phosphorous' *read* 'phosphorus'.
39. Between fourth and fifth line from bottom ; *insert*  
'<sup>44</sup> Beryllium chloride | 2·93 | 81·73 | 79·84 | 9·1 beryllium + 70·84 chlorine'.
41. At end of note 4 ; *insert* '<sup>44</sup> See Nilson and Pettersson, *Ber.* 17. 987'.
41. At end of notes ; *insert* 'V. Meyer (*Ber.* 17. 1335) has obtained numbers which seem to indicate that gaseous ferrous chloride at low temperatures consists of molecules of  $\text{Fe}_2\text{Cl}_4$ , and at high temperatures of molecules of  $\text{FeCl}_2$ '.
63. Line 20 from top ; before 'Kopp's hypothesis' *insert* 'With regard to' and *dele* from 'will be again' to 'meanwhile' (both inclusive).
76. At end of note 1 ; *add* 'also *ibid.* 17. 1335'.
78. In second column opposite BERYLLIUM ; *for* 'none' *read* ' $\text{BeCl}_2$ '.
90. *Note* ; *after* 'Book II. chap. II.' *insert* 'par. 189'.
148. *Note* ; *for* '*loc. cit.*' *read* '*Organic Chemistry*'.
190. *Note* ; *for* 'Book II. chap. II.' *read* 'Book II. chap. I.'
208. *Note* 1 ; *add* 'See also Report of the B. A. committee on Spectrum Analysis. *Brit. Ass. Reports* for 1880. 258 ; especially pp. 284—298'.
214. *Note* 1 ; to references to work on cryohydrates, *add* '18. 22'.
229. *Note* 1 ; *add* 'But see Carnelley, *Ber.* 17. 1357'.
269. *Note* 2 ; *dele* [2].
294. Third line from top ; *for* 'combination' *read* 'oxidation'.
297. Seventh line from top ; *for* 'term' *read* 'terms'.
300. Ninth line from bottom ; *for* '(stone or system)' *read* 'stone (or system)'.
324. Seventh line from bottom ; *for* ' $(\text{R}_2\text{R}_2\text{C})$ ' *read* ' $(\text{R}_2\text{R}_2)\text{C}$ '.
372. Seventh line from bottom ; *for* 'relation' *read* 'relations'.
451. *Note* ; *add* 'See also *ibid.* *Phil. Mag.* (5). 18. 233'.

“L'action chimique est réciproque : son effet est le résultat d'une tendance mutuelle à la combinaison ; on ne peut pas, à la rigueur, dire plutôt qu'un liquide agit sur un solide, qu'on ne peut dire que le solide agit sur le liquide : la commodité de l'expression fait transporter sans inconvénient toute l'action dans l'une des deux substances, quand on veut examiner l'effet de cette action plutôt que l'action elle-même.” BERTHOLLET.



## INTRODUCTORY.

**CHEMISTRY** is preeminently the science which concerns itself with the changes presented in material phenomena ; it is the science which attempts to classify the mutations that matter undergoes.

In the chemical examination of any kind of matter two questions have always pressed for answers:—What can this substance do? Of what is this substance composed? While attempting to answer these questions separately, and while thus more or less adopting two schemes of classification, chemists have for the most part recognised that no complete answer could be given to either question considered wholly apart from the other; hence the two methods of chemical investigation, and the two lines of chemical advance have generally been closely interwoven.

In older times a substance was said to be capable of doing this or that because it contained certain elements or essences; substances were classed together because of similarity of actions, but the points of resemblance on which classification was based were uncertain and undefined:—the conception of element was paramount. The substances in a class shewed many or a few points of resemblance because each member of the class contained the same element, and hence was a more or less perfect means for exhibiting the properties of that element. The ideas of composition and properties, as we now use these expressions, were both implied in the older conception of element.

If it be granted that the various forms of matter are vehicles for displaying the properties of a few elements, it follows that the addition or withdrawal of this or that element will probably suffice to change one into another form of matter. Hence arose the art of alchemy and the pursuit of the philosopher's stone. This pursuit resulted in the accumulation of many facts most of which could for some time be explained by aid of the one underlying general conception of element. But as facts accumulated the foundation was found to be too narrow to bear the structure raised upon it; a need was felt for minor explanations and for partial hypotheses. Observers began to contrast sour, acid substances with mild, tasteless, non-corrosive substances; hence arose the division of a large class of bodies into two minor classes, acids and alkalis. This classification when carried to completion produced the school of *iatro*-chemists, in whose hands chemical science became a branch of the art of medicine. But once again facts were observed which could not be explained by the theories of the medical chemists: the experimental method was recognised as alone leading to definite and trustworthy results in the examination of natural phenomena; but the experimental method, it was found, to be of value must be accurate, and to be accurate must be quantitative. Advance became rapid. The conception of element remained but in modified form, the distinction between alkali and acid remained, but proved to mean at once less and more than its originators supposed. Bodies were compared as to their actions and as to their compositions; the comparison led on one hand to the recognition of force exerted by one body on another, called affinity, and on the other hand to the recognition of ultimate forms of matter, called elements, of which all bodies are composed.

From this point the two broad paths of advance become more easily distinguished; advance is made by seeking answers to questions such as these:—What is the nature of the elements? What is the composition of compounds? Can the facts regarding elementary combinations be generalised? Advance is also made by pursuing inquiries indicated

by such questions as these :—What connection, if any, exists between the properties of elements and of compounds of these elements? What actions are these compounds capable of performing? And advance is also made by combining both methods of inquiry in seeking answers to such a question as this :—Why are the properties of these compounds such as they are observed to be?

At one time those chemists for whom the composition of compounds was all-important have been supreme; at another time the place of authority has been occupied by those who regarded function, or power of doing, as the essential subject of study. The greatest outcome of the work of the former school is the atomic hypothesis, now merged in the wider molecular theory of matter; the most important result of the studies of the latter school is the conception of chemical affinity; both have taken part in the development of the modern views regarding molecular structure and rational formulæ.

While assigning the credit of special advances to one of the two great schools of chemistry, we cannot but recognise that these advances have been made by the help of suggestions borrowed from the other; recent developments of the atomic theory cannot be separated from the rise of the unitary system, the latest hypotheses regarding the structure of molecules are connected with the subject of chemical affinity.

Eighty years ago Berthollet attempted to arrange the facts of chemical action under a general conception which should serve to connect chemical with physical changes; but the attempt was only partially successful because of the scanty supply of purely chemical data. General views of chemical action were soon abandoned for a study of the properties of the products of this action, but of late years many chemists have resumed the investigation of the general conditions of chemical action, and have obtained results which give good grounds for hoping that this study will throw light on the masses of facts already accumulated concerning compounds, and groups of compounds, and taken along with that method

of investigation which is based on a study of the composition of compounds, will lead to the establishment of chemistry as a branch of the science of dynamics.

The study of the motions of material bodies considered as accompanying mutual actions between these bodies belongs to the general science of dynamics. Phenomena presented by mutually acting bodies wherein the properties of these bodies are not profoundly modified, belong to the domain of physical science. Chemistry deals with those reactions between bodies wherein profound modifications in the properties of the bodies occur. Or, we may say that whereas physical science is concerned with the properties of this or that kind of matter considered for the most part apart from the action on it of other kinds of matter, chemistry is concerned with the mutual actions which occur between matter of different kinds whereby persistent changes in the properties of the reacting kinds of matter occur.

Chemistry furnishes problems for the solution of which physical and dynamical methods are applicable. Chemical science is ever tending toward abstract truths, i.e. truths involved in many phenomena although actually seen in none: but before she gains abstract truths chemistry amasses many general truths, i.e. 'truths which sum up many facts'.<sup>1</sup>

The chemist is set to solve the problem,—Why are the properties of bodies profoundly modified under certain conditions? In attempting to find a solution, he must divide the phenomena which he observes into their factors, and study each of these as far as possible independently of the others.

The chemist need not regard the methods pursued by those sciences which are more concrete than his own, although he may furnish them with subject-matter for investigation; inasmuch however as the science of matter and motion is a more abstract science than that of chemistry, he must seek help for his work in the methods of that science,

<sup>1</sup> The abstract and the general truths of chemistry are scarcely yet so differentiated as to allow of each class being considered separately. I do not purpose attempting more than a very rough separation in this book.

always remembering that this help is given to solve chemical problems, and that with purely physical problems, he, as a chemist, is not concerned<sup>1</sup>.

Pursuing then an almost purely analytical method the chemist finds that his subject branches off into two main divisions. The properties of bodies are modified:—he studies the relations between the new substances and those by the mutual action of which the new bodies were produced; but changes in the properties of bodies involve a consideration of the relative positions of the changing body and of other bodies,—involve the action of force:—he endeavours to elucidate the laws of action of this force.

The hypothesis that bodies consist of small parts—called molecules—in motion, is one of the lines along which dynamical science pursues its advance into the sphere of chemistry. The study of chemical phenomena is also brought within the pale of dynamical methods by the application to these phenomena of the general principles of the conservation and degradation of energy<sup>2</sup>. The latter (thermodynamic) method is more applicable to the study of the laws of chemical forces than of the properties of the substances depending on the actions of these forces, which properties have been chiefly elucidated by the help of the molecular theory.

We may indeed study relations between forces accompanying changes in the distribution of certain material magnitudes, which we may call molecules, without reference to what is generally known as the molecular theory of matter.

But it seems certain that no chemical phenomenon—and it is well for the student to bear in mind that the chemical part is always but one aspect of any natural occurrence—can be fully explained unless both methods of investigation are applied; unless the relations between the reacting bodies and the products of the reaction, and the relations between the forces exhibited in the phenomenon in question, are considered.

<sup>1</sup> Chemistry, being more concrete, is less exact than Physics; mathematical methods can scarcely as yet be applied to chemical data.

<sup>2</sup> See Clerk Maxwell: *Science Conferences at South Kensington*, 1876.



In the following pages an attempt is made to gather together the more important data on which the leading generalisations of chemistry are based, and in the light of this material to discuss these generalisations.

By the use of the terms *Chemical Statics* and *Chemical Kinetics* I endeavour to indicate, roughly, that the phenomena included under the first of these headings are on the whole those exhibited by chemical bodies or systems of bodies in equilibrium, while the phenomena classed together as chemical kinetics relate more to bodies or systems of bodies when chemically active.

It may seem pedantic to make use of terms having definite and precise significations when from the very nature of the facts they can be employed only in the broadest and roughest way. I only wish to indicate that the subject-matter of chemical science is considered in this book as divisible into two large parts, of which one comprises the facts and principles concerned, on the whole, with chemical composition, and the other those which, broadly speaking, relate to chemical action.

It will of course be found that chemical occurrences present, I think one may say always present, both statical and kinetical problems; the two sides of any chemical problem can scarcely be regarded apart, in the present state of knowledge at any rate, without danger; it may therefore be that phenomena ranked by one chemist as statical would by another be classed as kinetical.

I begin by considering the facts and principles roughly classed as statical, because although the study of kinetics seems naturally to precede that of statics, yet in chemistry our knowledge of composition is much in advance of our knowledge of action: I then consider the data and generalisations of so-called chemical kinetics; and lastly I endeavour to review some of those phenomena, explanations of which, generally only very partial explanations, can be gained, or hoped for, only by the help of both methods.

## BOOK I.

### CHEMICAL STATICS.

#### CHAPTER I.

##### ATOMS AND MOLECULES.

1. THE foundations of the atomic theory were laid in the later years of last century by the German chemist RICHTER<sup>1</sup>. The work of BERGMANN<sup>2</sup>, although of earlier date than that of Richter, cannot be regarded of equal importance as concerns the history of the atomic theory.

Richter studied the neutralisation of acids by bases, and of bases by acids, and shewed that a definite amount of acid (or base) always combines with a definite amount of base (or acid) when neutralisation is accomplished. By determining the weights of various bases neutralised by one and the same weight of each acid, and the weights of various acids neutralised by one and the same weight of each base, Richter was able to arrange many acids and bases in order of neutralisation. FISCHER<sup>3</sup>, in 1803, published the first table of chemical equivalents. Richter had given a series of numbers for each base expressing the quantities thereof which would neutralise 1000 parts of sulphuric, hydrochloric, nitric &c. &c. acids; Fischer saw that it was sufficient to attach a single number to each base and a single number to each acid, 1000 parts of sulphuric acid being adopted as the unit of neutralisation. Fischer's numbers expressed quantities of bases, or

<sup>1</sup> *Ueber die neueren Gegenstände der Chemie, 1791—1802: and Anfangsgründe der Stöchiometrie oder Messkunst chemischer Elemente, 1812.*

<sup>2</sup> *Chemische Werke, 3. 25 et seq.*

<sup>3</sup> In a note to Berthollet's *Essai de Statique Chimique*.

acids, which were of equal value so far as power to neutralise a constant weight of a certain acid or base was concerned<sup>1</sup>.

Foreshadowings of the atomic theory are to be found in a work by W. HIGGINS entitled *A comparative view of the Phlogistic and Antiphlogistic Theories, with Inductions* (1791) [see Henry's *Life of Dalton* p. 75 *et seq.*] but to DALTON is undoubtedly due the signal honour of introducing a clear and self-consistent theory regarding the composition and structure of chemical substances, a theory which in its essential points has stood the test of rigorous experimental verification, and has adapted itself to the wants of each successive school of chemical thought.

2. Dalton<sup>2</sup>, and others, found that elements were united in many compounds in fixed proportions by weight, and moreover that in certain compounds of one element with others the amount by weight of this element could be expressed by whole multiples of one fundamental number<sup>3</sup>. To account for these facts Dalton recalled the atomic theory of the Greek philosophers; but he introduced accuracy where there had been vagueness. From an interesting intellectual plaything Dalton's genius produced an exact scientific theory capable of experimental application.

Every chemical substance, simple or compound, is made up of atoms, or small undivided parts<sup>4</sup>;—the old hypothesis had gone nearly as far as this: Dalton added, the atom of every chemical substance has a definite weight, and although this weight cannot be determined, we nevertheless can determine the *relative weights* of the atoms of all bodies. It

<sup>1</sup> For more details regarding the work of Richter and Fischer, see Wurtz, *The Atomic Theory*, pp. 12—22.

<sup>2</sup> It is important to note that the atomic theory was conceived by Dalton in 1802 from considering the results of *physical* experiments: he distinctly states in a paper on the absorption of gases in liquids read to the Manchester Philosophical Society in that year that he had lately been prosecuting 'with remarkable success,' 'an inquiry into the relative weights of the ultimate particles of bodies.'

<sup>3</sup> For examples of this law of multiple proportions see Roscoe and Schorlemmer's *Treatise on Chemistry*, 1. pp. 60—65.

<sup>4</sup> Dalton's application of the term *atom* to the small *chemically* indivisible parts of compounds, seems to shew that he did not regard his atoms as absolutely indivisible; see *Life* by Henry, p. 88.

is only necessary to choose some substance as a standard, then the weight of the smallest quantity of any other substance which combines with the unit weight of the standard substance represents the weight of the atom of the combining substance in terms of the unit chosen.

As this point is of supreme importance it may be well that we should have Dalton's own words before us. In the *New System of Chemical Philosophy* (1808) after discussing the constitution of mixed gases, Dalton proceeds: 'When any body exists in the elastic state its ultimate particles are separated from each other to a much greater distance than in any other state; each particle occupies the centre of a comparatively large sphere, and supports its dignity by keeping all the rest, which by their gravity or otherwise are disposed to encroach upon it, at a respectful distance. When we attempt to conceive the *number* of particles in an atmosphere, it is somewhat like attempting to conceive the number of stars in the universe; we are confounded by the thought. But if we limit the subject, by taking a given volume of any gas, we seem persuaded that, let the divisions be ever so minute, the number of particles must be finite; just as in a given space of the universe the number of stars and planets cannot be infinite.

'Chemical analysis and synthesis go no further than to the separation of particles one from another, and to their reunion. No new creation or destruction of matter is within the reach of chemical agency. We might as well attempt to introduce a new planet into the solar system, or to annihilate one already in existence, as to create or destroy a particle of hydrogen. All the changes we can produce consist in separating particles that are in a state of cohesion or combination, and joining those that were previously at a distance.

'In all chemical investigations it has justly been considered an important object to ascertain the relative *weights* of the simples which constitute a compound. But unfortunately the inquiry has terminated here; whereas from the relative weights in the mass, the relative weights of the ultimate

'particles or atoms of the bodies might have been inferred, 'from which their number and weight in various other 'compounds would appear, in order to assist and to guide 'future investigations, and to correct their results. Now it is 'one great object of this work, to shew the importance and 'advantage of ascertaining the relative weights of the ultimate 'particles both of simple and compound bodies, the number of 'simple elementary particles which constitute one compound 'particle, and the number of less compound particles which 'enter into the formation of one more compound particle.

'If there are two bodies, *A* and *B*, which are disposed to 'combine, the following is the order in which combination 'may take place, beginning with the most simple: namely—

'1 atom of *A* + 1 atom of *B* = 1 atom of *C*, binary,  
 '1 " " *A* + 2 atoms " *B* = 1 " " *D*, ternary,  
 '2 atoms " *A* + 1 atom " *B* = 1 " " *E*, ternary,  
 '1 atom " *A* + 3 atoms " *B* = 1 " " *F*, quaternary,  
 '3 atoms " *A* + 1 atom " *B* = 1 " " *G*, quaternary.'  
 &c., &c.

Dalton then states the following rules respecting chemical synthesis, which he employed in determining the relative weights of the smallest chemically indivisible parts of compound bodies<sup>1</sup>.

'1st. When only one combination of two bodies can be 'obtained, it must be presumed to be a *binary* one, unless 'some cause appears to the contrary.

'2nd. When two combinations are observed they must be 'presumed to be a *binary* and a *ternary*.

'3rd. When three combinations are obtained, we may 'expect one to be a *binary*, and the other two *ternary*.

'4th. When four combinations are observed, we should 'expect one *binary*, two *ternary*, and one *quaternary*.' &c. &c.

'From the application of these rules,' Dalton says, 'to the 'chemical facts already well ascertained, we deduce the follow-

<sup>1</sup> By the 'smallest chemically indivisible part' of a substance is meant an amount such that, if divided, substances (or a substance) are produced different in properties from the original substance.

'ing conclusions: 1st. That water is a binary compound of 'hydrogen and oxygen, and the relative weights of the two 'elementary atoms are as 1 : 7 nearly. 2nd. That ammonia 'is a binary compound of hydrogen and azote, and the relative 'weights of the two atoms are as 1 : 5 nearly....In all these 'cases the weights are expressed in atoms of hydrogen each 'of which is denoted by unity.'

Two oxides of carbon were known to Dalton, containing according to him, 5·4 parts by weight of carbon combined respectively with 7 and with 14 parts by weight of oxygen: the first of these bodies, in accordance with Dalton's second rule, was considered to be a *binary*, and the second a *ternary* compound; the formulæ given were CO and CO<sub>2</sub>, respectively. [C = 5·4, O = 7.]

But Dalton's CO<sub>2</sub> might have been regarded as a compound of 2·7 parts by weight of carbon with 7 parts by weight of oxygen, in which case its formula would have been written CO [C = 2·7]; Dalton's CO would then have become C<sub>2</sub>O [C<sub>2</sub> = 5·4]. The atomic weight of carbon would be determined as 2·7 or 5·4 according as carbon monoxide or carbon dioxide was decided to be a *binary* compound.

At a later time it was said by some chemists that a binary compound is always more stable than a ternary; if this rule were applied to the case of the oxides of carbon, Dalton's number for the atomic weight of carbon would be confirmed<sup>1</sup>.

3. These examples illustrate the great shortcoming of the Daltonian theory: the atomic weights of Dalton are either multiples or submultiples of a certain number, but we cannot tell what multiple or what submultiple. Let the relative weights of two elements, hydrogen being taken as unity, which form a compound *B*, be  $Q$  and  $Q_1$ , and let the atomic weights of these elements be  $A$  and  $A_1$ , respectively, then  $Q : Q_1 :: nA : n_1A_1$ , where  $n$  and  $n_1$  are whole numbers. But inasmuch as the values of  $n$ ,  $n_1$ ,  $A$ , and  $A_1$  are unknown it is evident that analysis alone, aided by the Daltonian theory, cannot determine the atomic weights of the elements which compose the substance *B*.

<sup>1</sup> See especially Daubeny's *Atomic Theory* (2nd edition 1850), pp. 119—120.

This shortcoming in the theory could not be supplied without further data: Dalton distinctly states that in order to determine the number of elementary atoms in the atom of a compound a knowledge of the composition of many compounds of the given elements is required.

4. A few months after the announcement of Dalton's law of multiple proportions and atomic theory, GAY LUSSAC and HUMBOLDT<sup>1</sup> began their volumetric investigations which culminated three years later in the beautiful discovery of the former naturalist<sup>2</sup>, that gaseous substances unite in fixed volumetric proportions which may be simply expressed.

There is a constant simple relation, said Gay Lussac, between the volume of a gaseous compound and the volumes of its constituent elements. Let one volume be defined as the volume occupied by one part by weight of hydrogen, then the combining volume of any gaseous element is always expressed by a whole number, e.g. one volume of nitrogen combines with one volume of oxygen to form two volumes of nitric oxide; two volumes of hydrogen and one volume of oxygen combine to form two volumes of water-gas; one volume of nitrogen and three volumes of hydrogen form two volumes of ammonia, &c. &c. Condensation sometimes occurs, sometimes the volume of the compound is equal to the sum of the volumes of the combining elements.

This discovery appeared to add fresh arguments to the theory of Dalton. The ratios of the weights of these combining volumes of the elements, hydrogen being taken as unity, represent, it was said, the relative weights of the atoms of these elements; and the conclusion was drawn, 'equal volumes of gaseous substances, measured at the same temperature and pressure, contain equal numbers of atoms.'

5. Dalton however refused to accept Gay Lussac's generalisation, and regarded his experimental methods as untrustworthy. We cannot, I think, fail to be struck with the justness of Dalton's objection to the statement 'equal volumes contain equal numbers of atoms.' he argued somewhat as follows:—One volume of nitrogen and one volume

<sup>1</sup> *Journal de Physique*, 60. 129.

<sup>2</sup> *Mém. de la Soc. d'Arcueil*, 2. 207.

of oxygen form two volumes of nitric oxide; but one atom of nitrogen and one atom of oxygen form one atom of nitric oxide; therefore, had the above statement been correct, the volume of nitric oxide would have been equal to, not twice as great as the volume of oxygen or of nitrogen. So again, one atom of hydrogen and one atom of oxygen form one atom of water, according to Dalton's rules: but Gay Lussac shewed that two volumes of hydrogen combine with one volume of oxygen to produce two volumes of water-gas; hence the atom of hydrogen occupies twice the volume occupied by the atom of oxygen, and therefore the statement of Gay Lussac is incorrect. If Dalton's definition of atom and his rules regarding atomic synthesis are adopted Gay Lussac's statement that 'equal volumes contain equal numbers of atoms' must be abandoned.

6. The difficulty was removed by AVOGADRO<sup>1</sup>, who (in 1811) introduced the idea of two kinds of atoms:—'*molécules intégrantes*,' or as we should now say *molecules*; and '*molécules élémentaires*,' or as we should now say *atoms*.

The *molecules* of elements are decomposed in chemical processes, said Avogadro, and the *atoms* unite to form new compounds. '*Equal volumes of gases contain equal numbers of molecules*.' The reaction between nitrogen and oxygen inexplicable by Gay Lussac's law now becomes clear; each molecule of nitrogen and each molecule of oxygen divides into two parts, and these parts unite to form the new molecules of nitric oxide, hence there are twice as many molecules of nitric oxide produced as there were molecules of nitrogen or oxygen originally present.

By thus recognising a higher order of atoms, as it were, Avogadro reconciled Dalton's theory with Gay Lussac's results.

Ampère<sup>2</sup> in 1814 drew prominent attention to the hypothesis of Avogadro, and attempted by its help to explain the structure of crystals. But the hypothesis had come before the times were fully ripe.

<sup>1</sup> *Journal de Physique*, 78. 58: also *Essai d'une manière de déterminer les masses relatives des molécules élémentaires des corps*, &c.

<sup>2</sup> *Ann. Chim. Phys.* 90. 43.



7. WOLLASTON<sup>1</sup> accepted Dalton's theory but proposed to use the word *equivalent*<sup>2</sup> in place of atom. In his paper published in 1814 (*loc. cit.*) Wollaston drew up a table of equivalents which he thought would be serviceable to the practical chemist in determining the amount of an acid which would combine with a given weight of base, or the weight of precipitate obtainable in a given reaction, &c. He arranged his numbers on a scale with a slider attached, and adopted a mechanical contrivance for aiding the analyst in using the table. Although Wollaston employed the word equivalent in place of atom, his scale and table must be regarded as helping to extend the use of the atomic theory<sup>3</sup>. For the practical purpose which he had in view Wollaston did not deem it necessary to adopt any theory; at the same time he regarded the atomic weights of Dalton, especially the atomic weights of compounds, as too hypothetical, and he thought that equivalents were to be preferred for most purposes.

Wollaston referred his equivalent numbers to oxygen as 10: the amount by weight of any element which combined with 10 parts by weight of oxygen was regarded by him as the equivalent of that element. But the system of equivalents was liable to the same objection as had been urged against the system of atomic weights;—it was too vague.

(1) 7.5 parts by weight of carbon unite with 20 parts by weight of oxygen, said Wollaston, therefore the formula of the compound produced is  $\text{CO}_2$ .

(2) Again 7.5 parts by weight of carbon unite with 10 parts by weight of oxygen, therefore the formula of the compound produced is  $\text{CO}$ .

But he might also have said

(1) 3.75 parts by weight of carbon unite with 10 parts by weight of oxygen, and the formula of the product is  $\text{CO}$ ; and

(2) 7.5 of carbon unite with 10 of oxygen, therefore the formula of the compound is  $\text{C}_2\text{O}$ .

<sup>1</sup> *Phil. Trans.* for 1814, 1 *et seq.*

<sup>2</sup> Wollaston appears to have first used this term in 1808 (*Phil. Trans.*).

<sup>3</sup> See Cannizzaro, *C. S. Journal* [2], 10. 945.

It seemed impossible to determine the equivalent weight of carbon, just as in Dalton's system it was impossible to determine the atomic weight of carbon<sup>1</sup>.

If the unit of equivalency is 8 parts by weight of oxygen, what is the equivalent of copper? An electric current is passed through a voltameter and also through molten cuprous chloride; for every 8 parts by weight of oxygen set free in the voltameter 63·5 parts by weight of copper appear in the second vessel: cupric chloride is substituted for cuprous chloride, and now 31·75 parts of copper are eliminated for every 8 parts of oxygen. So in the compounds of copper and oxygen, we have in one case 63·5 of copper combined with 8 of oxygen, in the other 31·75 of copper with 8 of oxygen.

So long as the term equivalent was applied to acids and bases, or to oxides, it had a definite meaning. The amount of oxide which neutralised unit weight of standard acid was the equivalent of that oxide, because it was equal, so far as neutralising power went, to some other weight of another oxide. 'When we speak of the equivalent of a body,' said Gerhardt, 'we should always indicate to what other body, to what functions, to what properties, that equivalent corresponds<sup>2</sup>.' Richter shewed that there is a constant relation between the amount of oxygen in an oxide and that in the acid which neutralises this oxide: e.g., in sulphuric acid, he said, the oxygen is three times, and in nitric acid five times that in the oxide neutralised, &c. This rule was made general. Now the equivalent of aluminium was said to be 13·7: the formula of sodium sulphate, in accordance with Richter's rule, was written  $\text{NaO} \cdot \text{SO}_4$ ; hence the formula of aluminium sulphate should have been written  $\text{Al}_3\text{O} \cdot \text{SO}_4$ , ( $13 \cdot 7 \times \frac{3}{8}$  = amount of aluminium uniting with 8 parts by weight of oxygen); but the formula was almost invariably written  $\text{Al}_2\text{O}_3 \cdot 3\text{SO}_4$ , which is a departure from a strictly equivalent notation.

<sup>1</sup> Thus for iron we have the equivalents 28 and 18·6: for carbon, the equivalents 3, 4, 8, and 12: for nitrogen, 4·6 and 2·3: for oxygen, 8 and 16: for silicon, 7 and 3·5, &c. &c. Williamson, *C. S. Journal*, 22. 328.

<sup>2</sup> Quoted by J. J. Griffin in the *The Radical Theory in Chemistry*, p. 32.

Mohr (*Mechanische Theorie der Chemischen Affinität*) who strongly upheld an equivalent notation, admits (*loc. cit.* pp. 143—144) that no equivalency exists between the oxides  $RO$  and  $R_2O_3$ ; he also despairs of determining the equivalent of phosphoric acid. Those quantities of two substances are, he says, equivalent, which, by combination with other bodies, produce similar compounds; but he fails to define 'similar compounds,' or rather he admits the impossibility of such a definition.

That the weights of elements which mutually combine do not always represent equivalent quantities of these elements was gradually discovered; but the so-called equivalent notation assumed that these weights do represent equivalent quantities of the combining elements.

8. The systems of chemical notation founded respectively on the atomic weights of Dalton, and on the equivalents of Wollaston continued to hold divided sway over the minds of chemists<sup>1</sup>. A man of preeminent powers of classification was required.

The system of chemical classification and notation elaborated by JACOB BERZELIUS (1779—1848) was essentially electrical. The dualism of the Berzelian school was the logical development of the views of Lavoisier concerning salts, and of the hypothesis of Davy upon the relations between electrical and chemical actions<sup>2</sup>. At present, however, this part of the work of the great Swedish chemist does not specially concern us.

Berzelius recognised the necessity of extending the generalisations already made concerning the combinations of atoms. To say that when two elements, by combining together, form only one compound, that compound contains one atom of each

<sup>1</sup> The student who wishes to pursue this subject in greater detail may consult any of the older text-books, on *the laws of combination and atomic weights*, e.g. Turner's *Chemistry*, pp. 212—235; he will thus become persuaded how impossible it was to determine the values of atomic weights with certainty. Some interesting points especially regarding the proposal to give two equivalents, or atomic weights, to some of the elements will be found in Griffin's *Radical Theory*, pp. 30—43.

<sup>2</sup> For a brief notice of the system of Berzelius regarding the constitution of compounds see chap. II. pp. 108—111.

element, was, according to Berzelius, not fully warranted by facts.

To discover the laws which govern atomic combinations was the task that Berzelius proposed to himself. He argued that inasmuch as the number of compounds formed by the mutual actions of any two or three elements is evidently very limited, there must be certain laws expressing the conditions under which alone atoms combine.

Berzelius regarded Gay Lussac's law of gaseous combination—'equal volumes contain equal numbers of atoms'—as the most important of the generalisations made concerning atomic combinations, but he restricted the application of this law to elementary gases. He admitted that a compound gas might contain half, or even less than half as many atoms as were present in an equal volume of an elementary gas, he did not compare the atomic composition of elementary and compound gases; he thus evaded the objections urged by Dalton against the law of Gay Lussac, and at the same time he declined to accept the statement of Avogadro, 'equal volumes contain equal numbers of *molecules*.'

The ratios of the weights of the combining volumes of elementary gases were regarded by Berzelius as representing the ratios of the weights of the atoms of those elements; therefore to water, nitric oxide, and ammonia he gave the formulæ,  $\text{H}_2\text{O}$ ,  $\text{NO}$ , and  $\text{NH}_3$ , because two volumes of hydrogen unite with one volume of oxygen to form water, one volume of nitrogen unites with one volume of oxygen to form nitric oxide, and ammonia is produced by the union of one volume of nitrogen with three volumes of hydrogen.

But the volumetric method was of limited application to the problems of chemical synthesis. Berzelius attempted to state general rules with regard to the combinations of atoms in solid and liquid compounds. These rules referred chiefly to oxygen compounds which play so important a part in mineral chemistry wherewith Berzelius largely concerned himself. The most important of the Berzelian rules were three.

I. If an element form two oxides with twice as much oxygen by weight in one as in the other, that with the

smaller amount of oxygen is to be represented as a compound of one atom of element united with one atom of oxygen, and that with the larger quantity of oxygen as one atom of element combined with two atoms of oxygen.

II. If an element form two oxides, one of which contains one and a half times as much oxygen as the other, that with the less oxygen is to be represented as composed of one atom of element and one atom of oxygen, and the other compound as formed by the union of two atoms of element with three atoms of oxygen.

III. The amount of oxygen in an acid is a simple multiple of the amount of oxygen in any base with which the acid combines<sup>1</sup>, and this multiple generally also expresses the number of atoms of oxygen in the acid: thus in the case of sulphuric acid and potash, an amount of acid containing 24 parts by weight of oxygen combines with that amount of potash which contains 8 parts of oxygen, therefore, by the Berzelian rule, there are three atoms of oxygen in one atom of sulphuric acid. When nitric acid neutralises potash there are 40 parts of oxygen in the acid for every 8 parts in the base; therefore an atom of nitric acid contains five atoms of oxygen.

By the use of these rules Berzelius determined the formulæ of many metallic oxides and salts. While he was thus engaged, Dulong and Petit<sup>2</sup> announced their 'law of atomic heats'; and shortly afterwards Mitscherlich<sup>3</sup>, his 'law of isomorphism.'

Berzelius adopted both laws, and by their help<sup>4</sup>, along with his own rules, he drew up a table of atomic weights which in very many cases were almost identical with those now in general use.

<sup>1</sup> This had been stated by Richter many years before Berzelius: see *ante* p. 15.

<sup>2</sup> See p. 46.

<sup>3</sup> See pp. 65—71.

<sup>4</sup> Berzelius formulated the law of isomorphism in its bearing on the problem of determining atomic weights, thus (*Lehrbuch* 3rd ed., p. 98)—when one body is isomorphous with another, the number of atoms in which is known, then the number of atoms in the other is known also, because isomorphism is a mechanical consequence of identity of atomic structure.

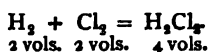
TABLE OF ATOMIC WEIGHTS. BERZELIUS<sup>1</sup>.

Arsenic	75'33	Manganese	57'02	Silver	216'61
Calcium	41'03	Sodium	46'62	Silicon	44'47
Chlorine	35'47	Phosphorus	31'43	Nitrogen	14'18
Iron	54'36	Mercury	202'86		
Iodine	123'2	Oxygen	16'00	Hydrogen	= 1.
Carbon	12'25	Sulphur	32'24		

Berzelius himself admits that the atomic weights determined by his rules are in many cases open to doubt (*Lehrbuch* 1st edition, vol. III. part i. pp. 87—102). Berzelius had a remarkable amount of tact; his rules were empirical but he balanced probabilities so well that he generally got the best possible result.

9. The separation which Berzelius made between formulæ of elementary and compound bodies, and his refusal to accept Avogadro's hypothesis while admitting Gay Lussac's generalisation, led him to a very curious result.

Two volumes of hydrogen, weighing 2, combine with one volume of oxygen, weighing 16, to form two volumes of water-gas. Therefore said Berzelius, *two atoms* of hydrogen combine with *one atom* of oxygen to form *one atom* of water-gas. But water contains less oxygen, relatively to hydrogen, than any other known oxide of hydrogen, therefore it is better to regard it as a compound of one atom of oxygen with *one double atom*, or with one atom itself composed of two equivalents, of hydrogen. Again in the formation of the lowest oxide of nitrogen two volumes of nitrogen combine with one of oxygen; but it is better to regard the nitrogen as composed of double atoms each occupying twice the volume of the atom of oxygen. Once more; hydrogen and chlorine combine in equal volumes, and the volume of the product—hydrochloric acid—is equal to the sum of the volumes of its constituents; but as the hydrogen atom was regarded by Berzelius as double, he wrote the atomic synthesis of hydrochloric acid as



<sup>1</sup> *Jahresberichte*, 1838. 73.

These results are evidently to be traced to the failure of Berzelius clearly to distinguish atom from equivalent, and to his refusal fully to accept the distinction between atom and molecule enunciated by Avogadro<sup>1</sup>.

To the great French chemists, DUMAS, GERHARDT and LAURENT, is chiefly due the introduction into general use of a system founded on Avogadro's distinction between atoms and molecules.

10. Dumas early accepted Avogadro's hypothesis; from the specific gravities of gases he deduced the relative weights of the molecules of these gases: in order to gain more information regarding molecular weights he introduced a new method for finding the specific gravities of gases. By this method he determined the molecular weight of sulphur to be 96, and that of phosphorus to be 124; but from the analogy of sulphur compounds with those of oxygen, from various chemical considerations regarding phosphorus compounds, and, I think we must add, from not keeping Avogadro's statement quite distinct from that of Gay Lussac, Dumas convinced himself that these results were incorrect. The molecular weight of mercury also seemed to be abnormal. Dumas knew of exceptions to the law of Dulong and Petit. Mitscherlich's law of isomorphism remained; but Mitscherlich had himself shewn that the same compound might assume more than one crystalline form, how then could trustworthy conclusions regarding atomic structure be deduced from so vague a law? Dumas, and indeed chemists generally, began to despair of the whole theory of atoms; they tried to find relief in equivalents, so called, and in spite of the many difficulties they gradually tended towards an equivalent notation, a notation which nevertheless they could not make thoroughly self-consistent, but which seemed to involve fewer hypotheses than that founded on the theory of atoms<sup>2</sup>.

L. Gmelin even regarded the law of fixity of composition

<sup>1</sup> For a more detailed account of the work of Berzelius on atomic weights see Ladenburg's *Entwicklungsgeschichte der Chemie*, pp. 89—100.

<sup>2</sup> For a general account of Dumas' influence on chemical theories see his *Leçons sur la Philosophie Chimique*, republished in 1878.

as only true under special conditions. When the affinity between two bodies is small, they may be united, said Gmelin, in almost any proportions, when the affinity is large they tend to combine in fixed proportions. A number may be given to each element representing the relative amount of that element which combines with other elements to form stable and well-marked compounds; this 'combining weight' may be *called* 'atomic weight,' but it is only a number. Gmelin adopted 8 as the combining weight of oxygen, 6 as that of carbon &c.: the formula of water on his system again became HO.

This notation was at best a compromise, and unsatisfactory, but it was very generally adopted for many years.

Inorganic chemistry had failed to introduce an accurate and satisfactory theory of chemical structure: it was now the turn of organic chemistry to attempt the task.

11. Among the most ardent followers of the new chemistry introduced by Dumas, were two men, whose names are ever to be associated as those of a brilliant pair of students of nature who died all too early for the work which seemed given them to do. Gerhardt and Laurent occupy a prominent place among the modern reformers of chemistry; they introduced order into chemical notation, and system, where system had been conspicuous by its absence<sup>1</sup>.

In criticising the system of so-called equivalent weights Gerhardt adopted the only true method, he studied actually occurring chemical reactions.

In a number of reactions between compounds of carbon in which carbon dioxide, water, and ammonia were produced, Gerhardt<sup>2</sup> found that when so-called equivalent weights of the reacting bodies were employed, the quantities of these three compounds evolved could always be represented by whole multiples of the formulæ  $C_3O_4$ ,  $H_2O$ , and  $NH_3$ , respectively, ( $C = 6$ ,  $N = 14$ ,  $O = 8$ ).

<sup>1</sup> Laurent's *Chemical Method* [Cavendish Society Publications] gives a general account of the more important work of these chemists.

<sup>2</sup> *J. für pract. Chemie*, 27. 439; and *Ann. Chim. Phys.* [3] 7. 129; and 8. 238.



He therefore concluded that these formulæ, rather than the commonly accepted formulæ  $\text{CO}_2$ ,  $\text{HO}$  (and  $\text{NH}_3$ ), must represent equivalent weights of the compounds in question.

Similarly he concluded that the equivalent formulæ of sulphur dioxide and carbon monoxide must be  $\text{S}_2\text{O}_4$  and  $\text{C}_2\text{O}$ , respectively: and arguing from these conclusions he thought himself justified in saying that the true equivalents of carbon, sulphur and oxygen are 12, 32, and 16, and not 6, 16, and 8 as generally adopted. Gerhardt likewise applied his acute reasoning powers to an examination of the arguments which determined Berzelius and others to adopt formulæ representing weights of four volumes of many carbon compounds; these arguments he proved to be fallacious.

Laurent examined the groundwork on which the systems of equivalent and atomic notation were based. His methods of reasoning were founded on experimentally determined facts, hence their irresistible force.

If formulæ are to represent equivalent weights of substances, then said Laurent, a standard must be adopted. But it had been frequently shewn that the quantities represented by so-called combining weights were not always mutually equivalent. Power of neutralising unit weight of standard substance might be adopted as the reaction on which to base the system, but this method could be applied only to a limited number of substances.

The idea of equivalency is associated with function; What is a given substance capable of doing?: this question must be answered before the equivalent of the substance can be determined. But in one action certain weights of two bodies may be equivalent, while altogether different weights of the same bodies are equivalent in another reaction.

Laurent affirmed that it was possible to found a systematic notation on equivalent weights assigned to the elements. Thus, in *ferrous* oxide 28 parts by weight of iron are combined with 8 parts by weight of oxygen,—let  $\text{Fe} = 28$ , then ferrous sulphate is represented by the formula  $\text{Fe}_2\text{SO}_4$ ; but in *ferric* oxide there are  $2 \cdot \frac{28}{3}$  (i.e. 18·6) parts by weight of iron for every 8 parts by weight of oxygen,—let  $\text{fe} = 18\ 6$ , then the

formula for ferric sulphate is  $\text{Fe}_2 \text{SO}_4$ : the formulæ  $\text{Fe}_2 \text{SO}_4$  and  $\text{Fe}_2 \text{SO}_4$  represent strictly equivalent quantities of the two sulphates of iron. So also if the composition of potassium-hydrogen sulphate is expressed by the formula  $\text{KHSO}_4$ , then, in a system of notation founded on equivalent weights, the composition of the double sulphate of potassium and aluminium is represented by the formula  $\text{K}_3 \text{Al}_3 \text{SO}_4$  ( $\text{Al} = 27.3$ ). But such a notation is inconvenient, and it frequently conceals most important facts; e.g. in a strictly equivalent notation the differences between monobasic and polybasic acids disappear.

Laurent returned to the generalisation of Avogadro and made that the basis of his system; he clearly distinguished between molecules and atoms, and he applied the law of equal volumes and equal numbers to molecules only. He admitted that apparent exceptions to the Avogadorean law existed—e.g. the molecules of sulphuric acid and salammuniac vapour appeared to occupy twice the volume occupied by the molecule of hydrogen;—but he said that this hypothesis generalised the facts better than any other which had been proposed.

Laurent founded his system on an atomic basis, and a fundamental point was the distinction between atom and molecule. He adopted formulæ representing two volumes: the facts of '*nascent*' action he explained by the conception of atoms as distinct from molecules. Molecule he defined to be 'the amount of a gaseous substance which occupies twice the volume occupied by an atom of hydrogen,' or, 'the smallest amount of a substance capable of taking part in a chemical reaction.' Atom he defined as 'the smallest amount of an element which enters into the composition of a compound.' Here we have the application of the term molecule to elements and compounds alike, while atom is used of elements only.

Equivalentents are the amounts of bodies which are of equal value in performing a stated action.

Gerhardt and Laurent adopted the laws of atomic heat and isomorphism as aids in determinations of atomic weights.

12. Chemical evidence in favour of the division of elementary molecules during chemical changes was accumulated by Brodie, Wurtz, Williamson and others, but the work of these chemists will be referred to in more detail when we come to speak of the chemical methods for determining molecular weights (see pp. 72—77).

Thus, at last, we have arrived at a clear separation between the meanings of the terms atom, molecule, equivalent.

The system now adopted in chemistry is essentially that of Gerhardt and Laurent; it is founded on the conception of atoms and molecules. Dalton's fundamental idea has been amply confirmed by modern research. We have maintained the idea of equivalency, but we no longer speak, as Wollaston did, of the equivalent of an element; we compare the elementary atoms among themselves and arrange them in groups all the members of each of which are equivalent in respect of a certain definite action they are capable of performing.

A true and fundamental conception once gained in science is never lost, it may be largely modified, it may even appear at times to be abandoned, but it develops slowly and bears much fruit at last.

The vicissitudes in the fortunes of a truly scientific idea are aptly illustrated by the history of the atomic theory. After a period of dormancy of more than 2000 years, the atomic theory was revived and rendered definite by Dalton, was firmly established on an experimental basis by Berzelius, was almost abandoned by the school founded by the same chemist, was rehabilitated and again nearly despaired of by Dumas, was largely advanced by Avogadro, was subdivided and its parts clearly distinguished by Gerhardt and Laurent, and is now the foundation-stone of a great and ever-increasing edifice.

13. Thus far I have dealt with the development of the atomic and molecular theory regarded almost entirely from the chemical point of view. So great however is the importance of clearly perceiving the position which this theory occupies in modern chemistry, and of realising the nature of the

physical evidence on which, in its more recent development, the theory so largely rests, that I must endeavour very briefly to give a sketch of that evidence, remembering always that it is as chemists, not as physicists, that we are interested in this subject.

There are two general theories of the structure of material substances: one assumes that apparently homogeneous bodies are really homogeneous throughout—a theory which is incapable of explaining the observed properties of matter—and the other, that apparently homogeneous bodies are possessed of a grained structure.

Viewed from a distance, a brick wall, or a body of soldiers, appears to be one reddish-coloured homogeneous mass, but a nearer observer sees that the wall is made up of distinct parts, that the company is composed of individual men.

The molecular theory supposes that were our senses sufficiently acute, we should see the grains or particles of which an apparently homogeneous mass of matter is composed.

The theory begins by assuming that any material body 'is made up of parts (each of which is capable of motion) 'and that these parts act on each other in a manner consistent 'with the principle of the conservation of energy<sup>1</sup>.' These parts are called molecules; the dynamical definition of a gaseous molecule is '*That minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motion of agitation of the 'gas*'.

This definition is entirely independent of chemical facts.

All the molecules of one element are of the same mass, else differences would be observed in the properties of an elementary gas, e. g. hydrogen, such differences arising from the separation of the gas into portions each more or less unlike the others.

The relations between the motions and the space occupied by these little parts, assuming their existence and mutual independence, may be dynamically deduced by the aid of a

<sup>1</sup> Clerk Maxwell, Article 'Atom' in *Encycl. Britannica*. (9th Ed.)

<sup>2</sup> *Ibid.*

theorem of Clausius, and, with a justifiable assumption as to the dynamical meaning of temperature, the equation thus arrived at expresses with considerable accuracy the relations actually existing between temperature and pressure, and volume, in the case of rarefied gases; the equation that is to say expresses the laws of Charles and of Boyle. When the gas is more condensed the equation ceases to express the relations existing between temperature and pressure, and volume; hence the theory asserts the existence in such a gas of mutual attractions or repulsions between the little parts, or molecules, it asserts that these parts are no longer mutually independent.

‘The hypothesis that a gas consists of molecules in motion, which act on each other only when they come together during an encounter, but which during the intervals between their encounters—which constitute the greater part of their existence—are describing free paths, and are not acted on by any molecular forces’, having been justified by dynamical reasoning, the next step is made by investigating mathematically the properties of such a system of molecules. And one deduction thus made is *‘If equal volumes of two gases are at equal temperatures and pressures, the number of molecules in each is the same, and therefore the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong’*.

This statement is of paramount importance to the chemist, inasmuch as on it is based his system of molecular weights. It is very necessary to bear in mind that this proposition is deduced by *dynamical reasoning* from a simple hypothesis as to the structure of matter, itself justified by many facts.

By analogous reasoning, various deductions are made from the theory, which express generalisations of experimentally determined facts concerning gaseous phenomena<sup>1</sup>.

Passing to more complex occurrences, the molecular theory

<sup>1</sup> Clerk Maxwell, Article ‘Atom’ in *Encycl. Brit.*

<sup>2</sup> *Ibid.*

<sup>3</sup> For some of the most important of these see Clerk Maxwell’s *Theory of Heat*, pp. 307—322 (6th edition).

gives a simple explanation of the diffusion of matter, diffusion of motion, and diffusion of heat in gases; these phenomena being regarded by the theory as dependent on the frequency of the molecular encounters, and on the nature of the actions between the encountering molecules.

The molecular theory has also been successfully applied to explain, broadly, many of the phenomena of evaporation, condensation, electrolysis, and spectroscopy.

To explain spectroscopic phenomena it is apparently necessary to assume molecules to be elastic substances, but elasticity is just the property of matter to explain which the molecular hypothesis was first assumed. The theory of 'vortex atoms,' developed by Sir William Thomson from the original conception of Helmholtz, explains spectroscopic facts—and generally those facts which must be explained by a successful molecular theory—better than any other which has yet been suggested. A short account of this theory will be found in the article 'Atom' in the last edition of the *Encyclopædia Britannica*, where we read 'The success of this theory in explaining phenomena does not depend on the ingenuity with which its contrivers "save appearances" by introducing first one hypothetical force and then another. When the vortex atom is once set in motion all its properties are absolutely fixed, and determined by the laws of motion of the primitive fluid which are fully expressed in the fundamental equation.'

Attempts have been made to determine the absolute size of molecules<sup>1</sup>, and although the results must be regarded as but rough estimates, nevertheless they shew that to measure molecules is a legitimate object of scientific investigation. The smallest portion of matter visible by the help of a good microscope may be taken to be a cube each side of which measures  $\frac{1}{4000}$ th of a millimetre in length; such a cube will contain—according to the rough measurements hitherto made—from 60 to 100 millions of molecules<sup>2</sup>.

<sup>1</sup> See especially Sir W. Thomson, *Nature* 1. p. 551, and also 28. pp. 203, 250, 274.

<sup>2</sup> Clerk Maxwell, *loc. cit.*

The foundations of a truly mathematical theory have been laid by Helmholtz and Thomson in their theory of vortex atoms; but, apart from this, the fact that the proposition commonly known as Avogadro's law may be deduced by dynamical reasoning from a simple hypothesis which admits, although as yet only to a limited extent, of the application of mathematical methods, and which is justified by a large number of physical facts, suffices to make that law of extreme importance.

Mathematical theories of physical phenomena in which the forces at work are thoroughly known, are complete, and are capable of making predictions which may afterwards be verified by experiment, or even of predicting phenomena which are altogether beyond the reach of experimental verification. When however the forces are but partly known, the theory may predict results but cannot give a complete account of the phenomena to which it is applied<sup>1</sup>. Now, we know very little of the forces at work in the phenomena called chemical, hence a mathematical theory of chemical action cannot as yet be formed. A beginning has been made in the knowledge of molecular forces, but until our knowledge is much extended, until we can generalise the conditions of molecular actions and reactions, and also of molecular decompositions and recompositions, we cannot expect to gain a complete mathematical theory of chemical action. At present we can use the molecular theory of matter only in a most general form, trying to make our deductions therefrom as accurate as possible, and always testing these deductions by experiment.

Attempts have recently been made to apply a more strictly dynamical method of reasoning than is presented by the molecular theory, to certain chemical phenomena; these will be referred to under the second main division of this book.

An atomic theory has been elaborated by the chemist; a molecular theory of matter has been propounded by the physicist, and has been advanced so far as to allow of wide conclusions being deduced therefrom by strictly dynamical

<sup>1</sup> See Thomson and Tait, *Treatise on Natural Philosophy*, 1. p. 445.

reasoning; no theory asserting the continuity of matter has been found capable of explaining the observed phenomena of matter; hence to accept the molecular theory, as, at present, the only feasible working hypothesis, is simply to obey the dictates of the scientific method.

14. *Equal volumes of gases contain equal numbers of molecules.*

Let us now consider one or two chemical reactions between gaseous substances.

Hydrogen combines with chlorine to form hydrochloric acid.

2 vols.                   "                   2 vols.                   "                   4 vols.                   "

But since equal volumes contain equal numbers of molecules, and since each molecule of hydrochloric acid contains both hydrogen and chlorine, it is evident that each molecule of hydrogen by combination with one molecule of chlorine produces not one but two molecules of hydrochloric acid.

So again,

Nitrogen combines with hydrogen to form ammonia.

2 vols.                   "                   6 vols.                   "                   4 vols.

Here again each nitrogen molecule has given rise to two molecules of ammonia. Hence it is evident that although the parts of a molecule of hydrogen, nitrogen, or chlorine 'do not' part company during the motion of agitation of the gas' to which the molecule belongs, these parts nevertheless do part company in those chemical reactions which are stated above. When various reactions between gaseous substances are studied this conclusion is found to hold good throughout a large range of chemical phenomena. Hence the chemist is obliged to recognise a portion of matter smaller than the molecule; this smaller portion of matter is the atom<sup>1</sup>.

In the above and in other reactions it is shewn that the molecules of hydrogen, nitrogen, and chlorine split into two parts when these molecules act chemically on each other or on other molecules; hence the molecules of these elements may be

<sup>1</sup> It is well to note that the molecular theory of matter as applied to chemical phenomena does not assert or deny the finite divisibility of matter. In *C. S. Journal* [2], 18. 501, there is a most interesting paper by Clerk Maxwell on 'The dynamical evidence of the molecular constitution of bodies.'



represented by the symbols  $H_2$ ,  $Cl_2$ , and  $N_2$  respectively. These symbols represent weights of equal volumes of the three elements; if one of these weights be taken as the unit, the other weights are evidently the weights of the molecules of the gases in question referred to this standard, because equal volumes contain equal numbers of molecules, and therefore 'the masses of the two kinds of molecules are in the same ratio as the densities of the gases to which they belong.'

Hydrogen is the universally adopted standard of reference for molecular weights.

The modern molecular theory of matter is not identical with the atomic theory of Dalton; it is based on evidence of a different kind, it is essentially a physical and dynamical theory, although strengthened by chemical arguments. The atomic theory of modern chemistry may be regarded as growing out of the application of reasoning founded on chemical facts to the molecular theory of matter.

Assuming 'Avogadro's law' and remembering that the hydrogen molecule divides into two parts in many chemical changes, we arrive at the practical definition of molecular weight.

*The molecular weight of a gas is the weight of that volume thereof which is equal to the volume occupied by two parts by weight of hydrogen.*

In determining the specific gravity of a gas it is easier, and less liable to error, to find the weight of the vessel filled with air than with hydrogen; the result is therefore stated as specific gravity referred to air as unity. Now the specific gravity of hydrogen is  $\cdot 06926$  [air = 1]; the molecular weight required is specific gravity referred to hydrogen as 2, hence if  $M$  = molecular weight, and  $d$  = specific gravity referred to air as unity,  $M = \frac{2 \cdot d}{\cdot 06926} = 28 \cdot 87 \cdot d$ . Hence the practical rule for determining the molecular weight of a gas:—

*Find the specific gravity, i.e. the ratio between the weights of equal volumes of the gas and air under the same conditions of temperature and pressure, and multiply this by 28·87.*

15. The following table presents the results hitherto obtained regarding the molecular weights of elementary gases.

[The numbers in column v are not always exactly equal to the products obtained in column iv; for an explanation see pp. 34—35.]

*Molecular weights of elementary Gases.*

I	II	III	IV	V
Name of element	Spec. gravity (air = 1)	Temp. of observation	(sp. gr.) × 28·87	Molecular weight
<sup>1</sup> Hydrogen	·06926	0°	2	2
<sup>2</sup> Nitrogen	0·9713	0°	28·04	28·02
<sup>3</sup> Oxygen	1·106	about 1400°	31·94	31·92
<sup>4</sup> " (ozone)	1·10563	0°	31·92	
<sup>5</sup> " (ozone)	1·658	—	47·86	47·88
<sup>6</sup> Sulphur	2·23	860°	64·4	63·96
<sup>7</sup> "	2·24	1040°	64·6	
<sup>8</sup> "	2·17	about 1400°	62·6	
<sup>9</sup> "	2·93	665°	84·6	?
<sup>10</sup> Chlorine	6·62	524°	191·1	191·88
<sup>11</sup> "	2·45	200°	70·73	70·74
<sup>12</sup> "	2·61	about 1000°	75·35	
<sup>13</sup> "	2·44	about 1200°	70·72	
<sup>14</sup> Cadmium	3·94	about 1000°	113·7	112·1
<sup>15</sup> Phosphorus	4·35	500°	125·6	123·84
<sup>16</sup> "	4·50	about 1000°	129·9	
<sup>17</sup> Arsenic	10·2	860°	294·5	299·6
<sup>18</sup> "	10·65	644°—668°	307·4	
<sup>19</sup> Bromine	5·54	100°	159·9	159·5
<sup>20</sup> "	5·38	100°	155·3	
<sup>21</sup> "	4·43	about 1500°	117·9	?
<sup>22</sup> Selenion	5·68	about 1400°	161·1	157·6
<sup>23</sup> "	6·37	about 1000°	183·9	?
<sup>24</sup> "	7·67	860°	221·4	236·4
<sup>25</sup> Mercury	6·96	about 1000°	200·93	199·8
<sup>26</sup> "	6·98	446°	201·5	
<sup>27</sup> "	7·03	424°	203·0	
<sup>28</sup> "	6·7	882°	193·4	
<sup>29</sup> Iodine	8·8	250°—450°	254·0	253·07
<sup>30</sup> "	8·72	185°	251·7	
<sup>31</sup> "	8·70	447°	251·2	
<sup>32</sup> "	8·72	about 1000°	251·7	
<sup>33</sup> "	8·84	250°	255·2	
<sup>34</sup> "	8·55	665°	246·8	?
<sup>35</sup> "	5·87	about 1100°	169·4	
<sup>36</sup> "	4·76	about 1500°	137·4	[? 126·53]
<sup>37</sup> Tellurium	9·08	about 1400°	262·1	255

<sup>1</sup> REGNAULT, *Compt. rend.* 20. 975.

<sup>2</sup> *Ibid.*, loc. cit.

<sup>3</sup> V. MEYER,

*Ber.* 12. 1426.

<sup>4</sup> REGNAULT, loc. cit.

<sup>5</sup> SORET, *Compt. rend.* 61.

The specific gravities of the vapours of potassium and sodium have been determined by Dewar and Dittmar (*Chem. News*, 27. 121), and by Dewar and Scott (*ib.* 40. 293): but the numbers are not given in this table because V. Meyer has shewn that the process made use of was not trustworthy (*Ber.* 13. 391).

16. So many determinations of molecular weights of compound gases have been made that an enumeration of all the results would be perplexing, and of no special value. The method is applicable to elements and compounds alike. The following numbers are given here as they illustrate a point of general importance.

*Specific gravities of certain compound gases.*

Name.	Sp. gr.	Temperature.
Phosphorus pentachloride	5.08	180°
"	4.99	190°
"	4.30	230°
"	3.69	290°
"	3.66	335°
Nitrogen tetroxide	2.80	29°
"	2.40	45°
"	2.03	66°
"	1.83	83°
"	1.50	151°

- 941 and 64. 904. <sup>6 and 7</sup> DEVILLE and TROOST, *Compt. rend.* 56. 891.  
<sup>8</sup> V. MEYER, *Ber.* 12. 1112. <sup>8a</sup> TROOST, *Compt. rend.* 95. 30.  
<sup>9</sup> DUMAS, *Ann. Chim. Phys.* (2) 50. 170. <sup>10</sup> LUDWIG, *Ber.* 1. 232.  
<sup>11</sup> V. MEYER, *Ber.* 13. 400. <sup>11a</sup> *Ibid. do.* 15. 2773 (mean of 5 experiments). <sup>12</sup> DEVILLE and TROOST, *Compt. rend.* 49. 239. <sup>12 and 14</sup> *Ibid. do.*, 56. 891. <sup>13</sup> *Ibid.*, *loc. cit.* <sup>16</sup> MITSCHERLICH, *Annalen* 12. 159.  
<sup>17</sup> *Ibid.*, *loc. cit.* <sup>18</sup> V. MEYER, *Ber.* 13. 406. <sup>19</sup> CRAFTS, *Compt. rend.* 90. 183. <sup>20, 21 and 22</sup> DEVILLE and TROOST, *loc. cit.* <sup>23</sup> V. MEYER, *Ber.* 13. 1107 and 1110 (mean of 6 experiments). <sup>24</sup> DUMAS, *Ann. Chim. Phys.* (2) 33. 337. <sup>25</sup> MITSCHERLICH, *loc. cit.* <sup>26</sup> BINEAU, *Compt. rend.* 49. 799.  
<sup>27</sup> V. MEYER, and MEIER and CRAFTS, *Ber.* 13. 868 (mean of 7 experiments). <sup>28</sup> DUMAS, *loc. cit.* <sup>29 and 30</sup> DEVILLE and TROOST, *loc. cit.* <sup>31</sup> V. MEYER, *Ber.* 13. 396. <sup>31a</sup> TROOST, *Compt. rend.* 95. 30. <sup>32</sup> V. MEYER, *Ber.* 13. 1115. <sup>33</sup> *Ibid. do.* 13. 1010.  
<sup>34</sup> DEVILLE and TROOST, *loc. cit.*

*Note to preceding table.* The expression 'specific gravity of a gas' will be employed to denote the specific gravity referred to air as unity: the expression 'vapour density of a substance' to denote the specific gravity of a substance in the gaseous state referred to hydrogen as unity.

Name.	Sp. gr.	Temperature.
Ferric chloride	11.39	350°
"	11.37	450°
"	11.01	620°
Arsenious oxide	13.80	570°
"	13.78	1400°

From these numbers, and from those of the previous table, it is apparent that the specific gravities of certain gases—elementary and compound alike—decrease as the temperature increases, while in the case of other gases the density is practically independent of the temperature; a limiting value is however generally found for the specific gravity of a gas.

It would therefore appear that a chemical substance may have more than one molecular weight; but if the molecule is the smallest part of a substance which exhibits the characteristic properties of that substance, this is equivalent to saying that certain substances when heated may pass through a succession of changes, each phase being marked by the existence of a distinct kind of matter. More accurate experiment has shewn that the vapours of phosphorus pentachloride and nitrogen tetroxide, at high temperatures, are mixtures of phosphorus trichloride and chlorine, and of nitrogen tetroxide and nitrogen dioxide ( $N_2O_4$  and  $NO_2$ ) respectively, so that at these temperatures we have to deal not with homogeneous vapours, but with mixtures of different gases, varying in composition at different moments. The connection existing between temperature and the densities of gaseous elements and compounds will be examined in more detail in a future chapter<sup>1</sup> (see Book II.).

The practical outcome of these considerations is that in determining a molecular weight the gas must be proved to be really a homogeneous substance, and not a mixture pro-

<sup>1</sup> Avogadro's law may be deduced from the molecular theory of matter, but inasmuch as this theory is based upon more or less inexact hypotheses, and is as yet but in an early stage of development, inasmuch also as the deductions made from it concerning gaseous laws are strictly applicable only to 'perfect gases,' it follows that Avogadro's law cannot be regarded, at present, as absolutely true. The laws of Boyle and of Charles, which are also deducible from the molecular theory, do not give a complete account of the relations of gases to temperature and pressure.

duced by the decomposing action of heat on the original substance; and, further, that the value obtained for the specific gravity must be constant throughout a considerable range of temperature.

17. In determining the density of a gas, especially if at a somewhat high temperature, many sources of error are present; the result cannot therefore be more than moderately accurate<sup>1</sup>. But experimental errors are more easily avoided in the determination of the combining weight of an element, that is, the quantity of the element found in combination with one part by weight of hydrogen, 7.98 parts by weight of oxygen, or 35.37 parts by weight of chlorine. Now it is evident that the molecular weight of an element must be equal to, or a multiple of its combining weight, and the molecular weight of a compound must be equal to the sum, or to a multiple of the sum of the combining weights of its constituent elements. Hence if the combining weight, and the specific gravity in the gaseous state of an element are carefully determined, we have the necessary data for an *accurate* determination of the molecular weight of that element; the combining weight being an accurately determined number, and the specific gravity deciding what multiple of that number represents the molecular weight. So also the data required for an *accurate* determination of the molecular weight of a compound are, the combining weights of the constituent elements, and the specific gravity of the com-

<sup>1</sup> Dumas' method for determining vapour densities is described in *Ann. Chim. Phys.* [2] **33**. 337; Gay Lussac's in Biot's *Traité de Phys.* **1**. 291; Hofmann's in *Ber.* **1**. 198; and Victor Meyer's *Ber.* **11**. 1868 and 2253. For criticisms on, and modifications of Meyer's method see *Ber.* **12**. 609 and 1112; **13**. 401, 851, 991, 1079, 1185, and 2019; **14**. 1727; and **15**. 137, 1161 and 2775: (in the last paper by V. Meyer [*Ber.* **15**. 2775] will be found an interesting and valuable criticism of the various methods for finding the Sp. Grs. of gases). See also *Ber.* **16**. 1051; also *C. S. Journal Trans.* for 1880. 491. Modifications of Dumas' method are described by Bunsen, see *Gasometrische Methoden*, 2nd ed. (1877), p. 172: also by Petterson and Ekstrand, *Ber.* **13**. 1191: and especially by Pawlewski, *Ber.* **16**. 1293. Thorpe [*C. S. Journal Trans.* for 1880. 147—150] has described a very complete method based on Hofmann's process. V. Meyer [*Ber.* **9**. 1260; and **10**. 2068] has described a method based on the displacement of mercury.

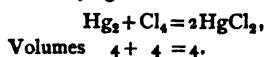
pound in the state of gas. Thus Regnault found for the specific gravity of chlorine the number 2·44, which multiplied into 28·87 gives 70·44. The combining weight of chlorine as most carefully determined by Stas is 35·37: now  $35·37 \times 2 = 70·74$ , which is very nearly equal to the molecular weight calculated from Regnault's numbers, hence 70·74 is taken to be the molecular weight of chlorine. Again, Thomson found the specific gravity of marsh gas to be 0·557, which multiplied into 28·87 gives 16·1 as approximately the molecular weight of this compound: the combining weight of carbon is 2·99 ( $H = 1$ ), and in marsh gas carbon and hydrogen are united in the proportion of 2·99 to 1, hence the molecular weight of this gas is 3·99 or a multiple thereof. But  $3·99 \times 4 = 15·96$ , therefore the molecular weight of marsh gas is taken to be 15·96.

The numbers in column v of the table on p. 31 represent the molecular weights of the various elements found by the method of specific gravity aided by determinations of the combining weights of the elements in question.

18. Facts have already been mentioned which on the assumption of the truth of Avogadro's law oblige us to conclude that in certain chemical reactions the molecules of the reacting elementary bodies undergo subdivision; indeed we are forced to the conclusion that the greater number of the elementary molecules are not homogeneous but are built up of smaller parts<sup>1</sup>. Now it is evident that the molecule of an element cannot contain less than two of these smaller parts or atoms, unless indeed the atom and molecule should be identical; and that the molecule of a compound cannot contain less than one atom of each of its constituent elements. Therefore if we determine the smallest amount by weight of an element in the molecule of any compound thereof, we shall have determined the maximum atomic weight of the element in question.

Hence we arrive at the following definition.

<sup>1</sup> Reactions are known in which it is not necessary to assume that subdivision of elementary molecules occurs, *e.g.*



*The maximum atomic weight of an element is the smallest quantity, in terms of hydrogen as unity, of that element in the molecule of any compound thereof.*

Molecular weight has been already defined as weight of two volumes of any gas referred to the weight of two volumes of hydrogen; hence the data which must be obtained before the maximum atomic weight of an element can be determined are, (1) specific gravity of a series of gaseous compounds of the element in question, and (2) careful analyses of these compounds. Suppose it is required to determine the maximum atomic weight of oxygen, such data as are indicated in the following table are obtained.

*Data for determining maximum atomic weight of oxygen.*

Name of compound	Weight of 2 volumes, as gas, referred to hydrogen	Analysis of these 2 volumes
Water	17.99	15.96 oxygen + 2 hydrogen
Carbonous oxide	27.96	15.96 " + 11.97 carbon
Carbonic dioxide	44.15	31.92 " + 11.97 "
Nitrous oxide	43.9	15.96 " + 28.02 nitrogen
Methylic alcohol	32.3	15.96 " + 11.97 carbon + 4 hydrogen
Methyl nitrate	76.2	47.88 " + 11.97 carbon + 3 hydrogen + 14.01 nitrogen
Nitric oxide	30.0	15.96 oxygen + 14.01 nitrogen
Sulphurous oxide	64.9	31.92 " + 31.98 sulphur
Sulphuric oxide	86.9	47.88 " + 31.98 "
Phosphorus oxychloride	155.9	15.96 " + 30.96 phosphorus + 106.11 chlorine
Osmium tetroxide	257	63.84 " + 198.6 osmium

If the smallest weight of hydrogen found in a molecule of any compound of that element is called one, then in no molecule of any of the compounds in this table is there less than 15.96 parts by weight of oxygen; this number is therefore adopted as the maximum atomic weight of oxygen.

19. The following table (taken for the most part from Lothar Meyer's *Die modernen Theorien der Chemie*) contains the most important data hitherto accumulated for determining the maximum atomic weights of the elements by the application of Avogadro's law.

*Data for determining maximum atomic weights\*.*

*Note.* The numbers expressing specific gravities of the gaseous compounds have been determined at various temperatures; the range of temperature has been sufficient to obviate errors due to changes of specific gravity accompanying changes of temperature [see ante, p. 33]; in many cases the number given is the mean of several estimations.

The numbers in column IV headed 'Molecular weight' are obtained by the method of specific gravities aided by determinations of the combining weights of the various elements, as explained on pp. 34-35.

I Name of compound	II Sp. gr. as gas	III Sp. gr. X 28.87	IV Molecular weight	V Analysis, stated in parts <i>per molecule</i> , hydrogen being taken as unity	
<sup>1</sup> Hydrofluoric acid	0.693	20.0	20.1	19.1 fluorine	+ 1 hydrogen
Hydrochloric acid	1.247	36.0	36.37	35.37 chlorine	+ 1 "
Hydrobromic acid	2.71	78.23	80.75	79.75 bromine	+ 1 "
Hydriodic acid	4.443	128.0	127.53	126.53 iodine	+ 1 "
Water	0.623	17.99	17.96	15.96 oxygen	+ 2 "
Sulphuric acid	1.191	34.4	33.98	31.98 sulphur	+ 2 "
Sulphurous oxide	2.247	64.9	63.90	31.98 "	+ 31.92 oxygen
Sulphuric oxide	3.01	86.09	79.86	31.98 "	+ 47.88 "
Sulphuryl chloride	4.67	134.8	134.64	31.98 "	+ 31.92 "
<sup>2</sup> Selenion hydride	2.795	80.54	80.8	78.8 selenion	+ 2 hydrogen
Selenious oxide	4.03	116.0	110.9	78.8 "	+ 31.92 oxygen
<sup>3</sup> Tellurium hydride	4.49	129.62	129.5	127.5 tellurium	+ 2 hydrogen
Ammonia	0.597	17.2	17.01	14.01 nitrogen	+ 3 "
Nitric oxide	1.039	30.0	29.97	14.01 "	+ 15.96 oxygen
Nitrogen dioxide	1.50	43.3	45.93	14.01 "	+ 31.92 "

\* It has not been considered necessary to give references to all the papers where full accounts of determinations of the specific gravities of the compounds in this table are to be found; most of the numbers have been for years considered as among the well established data of the science. Notes are appended giving references, &c. in all cases of especial interest, or where explanation of the numbers appears to be called for.



I Name of compound	II Sp. gr. as gas	III Sp. gr. × 26·87	IV Molecular weight	V Analysis, stated in parts <i>per molecule</i> , hydrogen being taken as unity	
Nitrosyl chloride	2·31	66·68	65·34	14·01 nitrogen	+ 15·96 oxygen + 35·37 chlorine
Phosphorous trihydride	1·15	33·1	33·96	30·96 phosphorus	+ 3 hydrogen
Phosphoric fluoride	2·19	63·23	126·46	30·96 "	+ 95·5 fluorine
Phosphorous chloride	4·88	140·9	137·07	30·96 "	+ 106·11 chlorine
Phosphorous iodide	14·46	417·1	410·55	30·96 "	+ 379·59 iodine
Phosphoryl chloride	5·40	155·9	153·03	30·96 "	+ 106·11 chlorine + 15·96 oxygen
Triphosphoryl chloride	5·88	169·7	169·05	30·96 "	+ 106·11 " + 31·98 sulphur
Triethyl-phosphine oxide	4·60	132·8	133·74	30·96 "	+ 15·96 oxygen + 71·82 carbon + 15 hydrogen
Arsenic trihydride	2·695	77·8	77·90	74·90 arsenic	+ 3 hydrogen
Arsenious chloride	6·30	181·9	181·0	74·90 "	+ 106·11 chlorine
Cacodyl chloride	4·56	131·7	140·2	74·9 "	+ 35·37 chlorine + 23·94 carbon + 6 hydrogen
Cacodyl cyanide	4·63	133·7	130·8	74·9 "	+ 14·01 nitrogen + 35·91 carbon + 6 hydrogen
Methyl arsenite	6·006	173·4	169·7	74·9 "	+ 47·88 oxygen + 35·91 carbon + 9 hydrogen
Arsenious iodide	16·1	464·8	454·5	74·9 "	+ 379·59 iodine
Antimonious chloride	7·8	224·7	226·1	120 antimony	+ 106·11 chlorine
Antimonious ethide	7·44	214·8	206·8	120 "	+ 71·82 carbon + 15 hydrogen
Bismuthous chloride	11·35	327·7	314·1	208 bismuth	+ 106·11 chlorine
Boron trifluoride	2·312	66·8	68·3	10·95 boron	+ 57·3 fluorine
Boron trichloride	{ 3·942 4·02	{ 113·8 116·0	{ 117·0 117·0	10·95 "	+ 106·11 chlorine
Boron tribromide	8·78	253·5	250·2	10·95 "	+ 239·25 bromine
Boron trimethide	1·93	55·7	55·9	10·95 "	+ 35·91 carbon + 9 hydrogen
Methane	0·555	16·0	15·97	11·97 carbon	+ 4 hydrogen
Methyl fluoride	1·186	34·3	34·10	11·97 "	+ 19·1 fluorine + 3 hydrogen
Methyl chloride	1·736	50·1	50·34	11·97 "	+ 35·37 chlorine + 3 "
Methyl bromide	3·253	93·9	94·72	11·97 "	+ 79·75 bromine + 3 "
Methyl iodide	4·883	141·0	141·50	11·97 "	+ 126·53 iodine + 3 "
Chloroform	4·20	121·3	119·08	11·97 "	+ 106·11 chlorine + 1 hydrogen

Carbon tetrachloride	{ 5.24	151.3	153.45	11.97 carbon	+ 141.48 chlorine
Carbon monoxide	{ 5.33	153.9	27.93	11.97 "	+ 15.96 oxygen
Carbon dioxide	0.908	27.96	43.89	11.97 "	+ 31.92 "
Carbon oxychloride	1.529	44.15	98.67	11.97 "	+ 15.96 " + 70.74 chlorine
Carbon oxysulphide	3.505	101.2	59.91	11.97 "	+ 15.96 " + 31.98 sulphur
Carbon disulphide	2.105	60.8	75.93	11.97 "	+ 63.96 sulphur
Hydrocyanic acid	2.645	76.4	26.98	11.97 "	+ 14.01 nitrogen + 1 hydrogen
Cyanogen chloride	0.948	27.4	61.35	11.97 "	+ 14.01 " + 35.37 chlorine
Cyanic acid	2.13	61.5	42.94	11.97 "	+ 14.01 " + 15.96 oxygen + 1 hydrogen
Methylic alcohol	1.50	43.3	31.93	11.97 "	+ 15.96 oxygen + 4 hydrogen
Methyl nitrate	1.12	32.3	76.86	11.97 "	+ 14.01 nitrogen + 3 hydrogen + 47.88 oxygen
Silicon fluoride	2.64	76.2	104.4	28 silicon	+ 76.4 fluorine
Silicon tetrachloride	3.57	103.0	169.5	28 "	+ 141.48 chlorine
Silicon tetriodide	5.94	171.5	534.1	28 "	+ 506.12 iodine
Silicon tetrithide	19.1	551.4	143.8	28 "	+ 95.76 carbon + 20 hydrogen
Silico-chloroform	5.13	148.1	135.11	28 "	+ 106.11 chlorine + 1 hydrogen
Titanic chloride	4.64	133.9	189.5	48 titanium	+ 141.48 "
Zirconium chloride	6.84	197.5	231.5	90 zirconium	+ 141.48 "
Stannic chloride	8.15	235.4	259.3	117.8 tin	+ 141.48 "
Stannic bromide	9.20	265.7	436.8	117.8 "	+ 319 bromine
Stannous chloride	7.9	458.0	186.2	117.8 "	+ 70.74 chlorine
Stannic ethide	6.45	186.2	233.6	117.8 "	+ 95.76 carbon + 20 hydrogen
Stannic triethyl chloride	8.02	231.6	240.0	117.8 "	+ 35.37 chlorine + 71.82 carbon + 15 hydrogen
Stannic triethyl bromide	8.43	243.4	284.4	117.8 "	+ 79.75 bromine + 71.82 " + 15 "
Stannic triethyl iodide	9.92	286.4	289.2	117.8 "	+ 126.53 iodine + 35.91 " + 9 "
Thallous chloride	10.33	298.2	239.0	203.64 thallium	+ 35.37 chlorine
Lead tetramethide	8.22	237.4	266.3	206.4 lead	+ 47.88 carbon + 12 hydrogen
Lead dichloride	9.6	277.2	277.2	206.4 "	+ 70.74 chlorine
Zinc chloride	9.5	274.2	135.6	64.9 zinc	+ 70.74 "
Zinc methide	4.6	132.8	94.8	64.9 "	+ 23.94 carbon + 6 hydrogen
Zinc ethide	3.29	95.0	122.8	64.9 "	+ 47.88 " + 10 "
Cadmium bromide	4.62	123.0	271.5	112 cadmium	+ 159.5 bromine
	9.25	267.0			

I Name of compound	II Sp. gr. as gas	III Sp. gr. x 28.87	IV Molecular weight	V Analysis, stated in parts <i>per molecule</i> , hydrogen being taken as unity
Mercury dimethide	8.29	239.4	229.7	199.8 mercury
Mercury diethide	9.97	287.8	257.7	199.8 " + 23.94 carbon + 6 hydrogen
Mercurous chloride	8.3	239.6	235.17	199.8 " + 47.88 " + 10 "
Mercuric chloride	9.8	283.0	270.5	199.8 " + 35.37 chlorine
Mercuric bromide	12.16	351.0	359.3	199.8 " + 70.74 "
Mercuric iodide	16.2	468.0	452.9	199.8 " + 159.5 bromine
Osmium tetroxide	8.9	257.0	257.0	199.8 " + 253.06 iodine
Chromium oxychloride	{ 5.55 5.9	{ 159.0 170.0 }	155.1	193 osmium + 63.84 oxygen
Indium chloride	7.87	227.2	219.51	52.4 chromium + 31.92 " + 70.74 chlorine
Molybdenum pentachloride	9.46	273.0	272.7	113.4 indium + 106.11 chlorine
Tungsten pentachloride	12.7	366.0	360.5	95.8 molybdenum + 176.85 "
Tungsten hexchloride	13.2	382.0	395.8	183.6 tungsten + 176.85 "
Tungsten oxychloride	11.84	342.0	341.0	183.6 " + 212.22 "
Vanadium tetrachloride	6.69	193.0	192.7	183.6 " + 15.96 oxygen + 141.48 chlorine
Vanadium oxychloride	6.11	176.0	173.3	51.2 vanadium + 141.48 chlorine
Niobium pentachloride	9.6	277.0	270.9	51.2 " + 15.96 oxygen + 106.11 chlorine
Niobium oxychloride	7.88	228.0	216.1	94.0 niobium + 176.85 chlorine
Tantalum pentachloride	12.9	372.0	358.9	94.0 " + 15.96 oxygen + 106.11 chlorine
Uranium tetrachloride	13.3	383.9	381.5	182.0 tantalum + 176.85 chlorine
Uranium tetrabromide	19.46	561.8	559.0	240.0 uranium + 141.46 "
Ferric chloride	11.24	324.5	324.6	240.0 " + 319 bromine
Aluminium chloride	9.35	270.0	266.3	111.8 iron + 212.22 chlorine
Aluminium bromide	18.6	537.0	532.5	54.04 aluminium + 212.22 "
Aluminium iodide	27.0	780.0	813.2	54.04 " + 478.5 bromine
Cuprous chloride	6.99	201.8	197.5	54.04 " + 759.18 iodine
Galic chloride	11.9	343.6	350.2	126.8 copper + 70.74 chlorine
				138.0 gallium + 212.22 "



*Notes to the preceding Table.*

<sup>1</sup> The density of hydrofluoric acid was determined indirectly by Gore (*Phil. Trans.* for 1869. 173) at 100°. Mallet (*Amer. Chem. Journal* 3. 189) by directly weighing 1 litre of the gas at 30° found the specific gravity to be 1.42, which gives a molecular weight of 41.02. The molecular weight of this gas therefore decreases as temperature increases.

<sup>2 and 3</sup> Indirectly determined by Bineau (*Ann. Chim. Phys.* [2] 68. 424); two volumes of each hydride when decomposed by metal yielded 2 vols. of hydrogen, 78 parts by weight of selenium in one case, and 128 parts by weight of tellurium in the other being produced.

<sup>4</sup> At a temperature slightly above its boiling point the specific gravity of gaseous stannous chloride points to the molecular weight 377; but at 200° higher the specific gravity is as given in the table; this gas therefore, like hydrofluoric acid, has two molecular weights: see Meyer and Züblin (*Ber.* 13. 811).

<sup>5</sup> There is some doubt whether the vapour of mercurous chloride does or does not contain mercury and mercuric chloride: the number in the table is from a paper by Fileti, who states that by vaporising a mixture of the two chlorides of mercury, the protochloride remains undissociated (see abstract of Fileti's paper in *C. S. Journal Abstracts* for 1882. 466).

<sup>6</sup> *Chromium hexfluoride* ( $\text{CrF}_6$ ) is frequently mentioned in text-books as a gaseous compound of chromium; the evidence in favour of the existence of a definite fluoride of chromium is meagre, no determinations of its density (if it exists) have been made; see Unverdorben (*Pogg. Ann.* 7. 311).

<sup>7</sup> Odling [*Phil. Mag.* [4] 29. 316] gave the specific gravity of aluminium tetramethide at temperatures above 200° as 2.5, and at 130° as 5.0; but it is undecided whether the gas at 200° was homogeneous or a mixture of the products of decomposition by heat of molecules existing at lower temperatures (see Wanklyn *loc. cit.* 313 and Williamson *do.* 395). If the gas at 200° was really homogeneous, we should have  $2.5 \times 28.87 = 72.5$  as the molecular weight of aluminium tetramethide, and this quantity of the gas contains 27.3 aluminium + 35.91 carbon + 9 hydrogen (= 72.21).

<sup>8</sup> At 450° the sp. gr. of the vapour of gallic chloride is 7.8, and at the same temperature in presence of an indifferent gas acting as diluent, it is 6.6: the gas dissociates under these conditions. (See Lecoq de Boisbaudran, *Compt. rend.* 93. 294, 329 and 815.)

The maximum atomic weights deduced from these data may in many cases be regarded with a large degree of probability as the true atomic weights of the elements. The greater the number of gaseous compounds of an element analysed, the greater is the probability that the number which represents the smallest amount of that element in two volumes of any of these compounds is the true atomic weight of the element.

20. When the atomic and molecular weights of an element are known, the *atomicity of the molecule*, i.e. the number of atoms in the molecule, is known.

In the following table the molecules of the elements, so far as the relative weights of these have been determined by the method founded on Avogadro's law, are classified in accordance with their atomicity.

*Atomicity of Elementary Molecules<sup>1</sup>.*

<i>Monatomic</i>	<i>Diatomic</i>	<i>Triatomic</i>	<i>Tetratomic</i>	<i>Hexatomic</i>
Cadmium Mercury Iodine (at about 1500°) (? Bromine at about 1800°)	Hydrogen Chlorine Bromine Iodine (200° to about 1000°) Oxygen Sulphur (at 800° and upwards) Selenion (at 1200° and upwards) Tellurium Nitrogen	Oxygen (ozone) Selenion (700° to 800°)	Phosphorus Arsenic	Sulphur (450° to about 550°)

The molecules of the majority of the elements in this table are diatomic, but inasmuch as the molecular *and* atomic weights of only 13 elements have been determined it is impossible to say whether a majority of all the elementary molecules contain each two atoms. It ought also to be observed that of the 13 elements in the table, five have more than one molecular weight, and therefore exhibit the phenomenon of varying atomicity.

The table contains two well-defined metals, cadmium and mercury; the molecules of these elements are monatomic, and hence are of a simpler structure than the molecules of those elements which possess in a marked manner the properties summed up in the term nonmetal.

<sup>1</sup> This table shews that many elementary gases have complex structures; hence arise difficulties in forming accurate physical conceptions of actions and reactions among the parts of these structures. This will be again referred to when dealing with atomic heats (see pp. 64—5).

21. Chemical formulæ for the most part profess to represent not only the elementary composition, but also the relative weights of the molecules, of the bodies formulated: but unless some method for determining molecular weights other than that founded on Avogadro's law is adopted, it is evident from the data in the table on pp. 37—40 that the majority of the formulæ employed in mineral chemistry cannot be said to be certainly molecular formulæ. Thus analysis shews that 17·96 parts by weight of water contain 15·96 parts of oxygen and 2 parts of hydrogen; analysis also shews that 58·37 parts by weight of sodium chloride contain 23 parts of sodium and 35·37 parts of chlorine. The specific gravity of water vapour shews that the molecular weight of this compound is about 18, hence—assuming the atomic weight of oxygen to be 15·96—the molecular formula is written  $\text{H}_2\text{O}$  (17·96). But no determination of the density of sodium chloride vapour has yet been made; hence the molecular weight *may* be about 59, or it may be a multiple of this number (assuming the atomic weights of sodium and chlorine to be known), and hence the formula  $\text{NaCl}$  (58·37) is not necessarily molecular, and is therefore not strictly comparable with the formula  $\text{H}_2\text{O}$ .

Even if a formula does express the relative weight of the molecule of the body formulated it is well to remember that it is the weight of the gaseous molecule which is thus expressed; the formula does not necessarily also represent the relative weight of the molecule of the same body when solid.

As a general rule, the melting and boiling points of substances with large molecular weights are high; thus in any homologous series of hydrocarbons the boiling and melting points increase with increase of molecular weight<sup>1</sup>; the same connection between these constants is noticed in many series of oxides, e.g. the oxides of nitrogen<sup>2</sup>. It would therefore appear probable that the molecular weight of a solid is greater

<sup>1</sup> Thus,  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ ,  $\text{C}_7\text{H}_{16}$ ,  $\text{C}_8\text{H}_{18}$ ,  $\text{C}_9\text{H}_{20}$ ,  $\text{C}_{10}\text{H}_{22}$  &c.  
B. P. =  $1^\circ$      $38^\circ$      $70^\circ$      $99^\circ$      $124^\circ$      $148^\circ$      $167^\circ$  &c.

<sup>2</sup>         $\text{NO}$                  $\text{N}_2\text{O}$                  $\text{N}_2\text{O}_3$                  $\text{N}_2\text{O}_4$                  $\text{N}_2\text{O}_5$   
gaseous at  $-110^\circ$ , B. P. =  $-88^\circ$ , about  $-20^\circ$ ,  $22^\circ$ , M. P. =  $30^\circ$ .

than that of the same substance when in the state of gas. So also, as a rule, the action of heat produces molecules of less, from those of greater weight. Thus  $\text{N}_2\text{O}_4$  which exists at low temperatures becomes  $\text{NO}_2$  when heated (see numbers on p. 32); so  $\text{S}_8$  exists at  $500^\circ$ , but  $\text{S}_2$  at  $1000^\circ$ : at temperatures above  $300^\circ$  the molecule  $\text{O}_2$  decomposes into  $\text{O}$ . Reactions are known in which heat appears to favour the production of molecules of greater weight and complexity than those previously existing; but these more complex molecules only mark intermediate stages towards the formation of less complex and comparatively lighter molecules. Thus the action of heat on sodium-hydrogen sulphate is generally formulated in two stages, (1)  $2\text{NaHSO}_4 = \text{Na}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$ : (2)  $\text{Na}_2\text{S}_2\text{O}_7 = \text{Na}_2\text{SO}_4 + \text{SO}_3$ . So also when mercuric cyanide is decomposed by heat molecules of cyanogen are produced, having the formula  $(\text{CN})_n$  where  $n > 2$ , but at  $800^\circ$ — $900^\circ$  these are dissociated into the lighter molecules  $\text{C}_2\text{N}_2$ . Lead monoxide  $(\text{PbO})_n$  when heated forms the heavier oxide  $(\text{Pb}_3\text{O}_4)_n$ , &c.: in many of these cases however we are not certain that the formulæ employed represent the relative weights of molecules.

The physical phenomena presented by liquids and solids cannot be expressed by such comparatively simple generalisations as those which express the properties of gases; the molecular phenomena of the former classes of bodies are evidently more complex than those of the latter class. Great caution must therefore be used in applying deductions made from the study of the molecular phenomena of gases to solid or liquid bodies<sup>1</sup>.

22. The following table gathers together the results of the observations recorded in the table on pp. 37—40, so far as regards the maximum atomic weights of elements determined by the application of Avogadro's law:

<sup>1</sup> The comparison of the molecular phenomena of gases with those of solids and liquids will be considered more fully in a future chapter.

*Maximum atomic weights of elements. (AVOGADRO'S law.)*

Name	Maximum atomic weight	Name	Maximum atomic weight	Name	Maximum atomic weight
Hydrogen	1	[Aluminium	54·04] <sup>1</sup>	Iodine	126·53
Boron	10·95	Zinc	64·9	[Copper	126·8] <sup>1</sup>
Carbon	11·97	Arsenic	74·9	Tellurium	127·5
Nitrogen	14·01	Selenium	78·8	[Gallium	138] <sup>1</sup>
Oxygen	15·96	Bromine	79·75	Tantalum	182
Fluorine	19·1	Zirconium	90	Tungsten	183·6
Silicon	28	Niobium	94	Osmium	195 (?)
Phosphorus	30·96	Molybdenum	95·8	Mercury	199·8
Sulphur	31·98	[Iron	111·8] <sup>1</sup>	Thallium	203·64
Chlorine	35·37	Cadmium	112	Lead	206·4
Titanium	48	Indium	113·4	Bismuth	208
Vanadium	51·2	Tin	117·8	Uranium	240
Chromium	52·4	Antimony	120		

About half of the known elements are found in this table.

Some method other than that based on the determination of the specific gravities of gaseous compounds must if possible be discovered for finding the atomic weights of the elements.

23. In his *New System of Chemical Philosophy*\* (pp. 70—75), Dalton discusses hypotheses regarding the quantities of heat contained in various elastic fluids, and decides in favour of that which asserts 'the quantity of heat belonging to the ultimate particles of all elastic fluids must be the same under the same pressure and temperature.' From this Dalton deduced the corollary 'the specific heats of equal weights of any two elastic fluids are inversely as the weights of their atoms or molecules.' The values of very few specific heats had been determined when Dalton wrote, and therefore he did not possess data sufficient to test the justness of his general principle. Dalton calculated the theoretical specific heats of various gases by the aid of the above corollary, employing atomic weights determined by himself. Regarding the table of numbers thus obtained he remarks 'upon the whole there is not any established fact in

<sup>1</sup> Especial reference will be made to those elements in brackets in a later paragraph: see p. 56.

<sup>2</sup> Published in 1808.



'regard to the specific heat of bodies, whether elastic or fluid, that is repugnant to the above table so far as I know; and it is to be hoped that some principle analogous to the one here adopted may soon be extended to solid and liquid bodies in general.'

In 1819 a paper by Petit and Dulong appeared in the *Annales de Chimie et Physique* [10. 395], containing the results of determinations of the specific heats of thirteen solid elements, viz. copper, gold, iron, lead, nickel, platinum, sulphur, tin, zinc, bismuth, cobalt, silver, and tellurium. A nearly constant product was obtained by multiplying the specific heats of the nine elements from copper to zinc, in this list, by the then generally accepted atomic weights of these elements, and the specific heat of bismuth, cobalt, silver, and tellurium by a sub-multiple of the accepted atomic weight of each of these elements. Generalising from these results the French physicists concluded that 'the atoms of all the simple bodies have exactly the same capacity for heat.'

The introduction of more accurate methods for determining specific heats has necessitated considerable alterations in many of the numbers to be found in the original paper of Petit and Dulong, nevertheless their general conclusion remains, although it cannot now be stated in terms quite so absolute as those used by its promulgators.

24. In 1831 F. Neumann<sup>1</sup> published determinations of the specific heats of various solid compounds, chiefly of naturally occurring minerals, and deduced the general statement, 'The amounts of chemically similar compounds expressed by their formulæ possess equal specific heats.'

A few years later (1833—4) Avogadro<sup>2</sup> detailed measurements of the specific heat of carbon, and of various compound substances, and drew certain general conclusions therefrom; he spoke of those atomic weights which were deduced from measurements of specific heats as the weights of thermal atoms (*atomes thermiques*).

<sup>1</sup> *Pogg. Ann.* 23. 1. Neumann measured the specific heats of 8 carbonates, 4 sulphates, 4 sulphides, 5 oxides of the type MO, and 3 of the type M<sub>2</sub>O<sub>3</sub>.

<sup>2</sup> Published in condensed form in *Ann. Chim. Phys.* [2] 55. 80: and 57. 113.

R. Hermann<sup>1</sup> made a number of determinations of specific heats, and from these deduced the combining weights of several elements. The weights thus obtained were in some cases different from the Berzelian weights then in general use. Hermann supposed that the specific heat of certain elements, e.g. sulphur and oxygen, varies according as the element is in the free state or in combination with other elements.

Regnault<sup>2</sup>, in a series of classical memoirs added much to our knowledge of specific heats, and gave a general confirmation to the laws of Dulong and Petit, and of Neumann. He arranged a table of so-called thermo-atomic weights: (see table).

*Regnault's Thermo-atomic weights.* [See KOPP, *loc. cit.*]

Al = 13·7	Cr = 26·1	Mn = 27·5	Se = 39·7
Sb = 61	Co = 29·4	Hg = 100	Ag = 54
As = 37·5	Cu = 31·7	Mo = 48	Na = 11·5
Ba = 68·5	F = 9·5	Ni = 29·4	Sr = 43·8
Bi = 105	Au = 98·5	N = 7	S = 16
B = 10·9	I = 63·5	Os = 99·6	Te = 64
Br = 40	Ir = 99	Pd = 53·3	Tl = 102
Cd = 56	Fe = 28	P = 15·5	Sn = 59
Ca = 20	Li = 3·5	Pt = 98·7	Ti = 25
C = 12	Pb = 103·5	K = 19·5	W = 92
Cl = 17·75	Mg = 12	Rh = 52·2	Zn = 32·6

Garnier<sup>3</sup> (in 1852) further generalised the relations between formula and specific heat of solid compounds; and Cannizzaro<sup>4</sup> advanced somewhat the generalisation of Garnier.

The Garnier-Cannizzaro generalisation may be stated thus:  $\frac{A \cdot C}{n} = \text{constant}$  (about 6·4), where A = formula-weight of a compound, C = specific heat of same compound, and n = number of elementary atoms in the formula.

<sup>1</sup> *Nouveaux Mémoires de la Société Impériale des Naturalistes de Moscou* (1834).

2. 137.

<sup>2</sup> *Ann. Chim. Phys.* [2] 63. 5. [3] 1. 129: 9. 322: 26. 261 and 268: 38. 129: 44. 257: 63. 5.

<sup>3</sup> *Compt. rend.* 38. 278: 37. 130.

<sup>4</sup> *Il Nuovo Cimento* 7. 321; Abstract in *Bull. Soc. Chim.* for 1868. 171.

25. Kopp<sup>1</sup> has gathered together most of the trustworthy results of specific heat determinations, and added many of his own, besides discussing the whole subject in detail.

*Table of Specific Heats of the Elements<sup>2</sup>.*

Name	Spec. heat	Temp.	Atomic weight	Sp. ht. x at. wt.	Observer
Lithium	0·941		7·01	6·6	Rg.
<sup>1</sup> Beryllium	0·58	250°	9·08	5·1	
<sup>2</sup> Boron	? 0·5	about 1000°?	10·9	5·5	Wb.
<sup>3</sup> Carbon	0·463	980°	11·97	5·5	Wb.
Sodium	0·293	- 34° to + 7°	23	6·7	Rg.
Magnesium	0·245		24	5·9	Kp.
"	0·25		"	6·0	Rg.
Aluminium	0·202		27·02	5·5	Kp.
"	0·214		"	5·8	Rg.
"	0·225		"	6·1	Mt.
<sup>4</sup> Silicon	0·203	232°	28	5·7	Wb.
Phosphorus (cryst.)	0·174	- 78° to + 10°	30·96	5·4	Rg.
"	0·189		"	5·9	Rg.
"	0·202		"	6·2	Kp.
" (red)	0·170		"	5·3	Rg.
Sulphur	0·188		31·98	6·0	D.P.
" rhombic	0·163		"	5·2	Kp.
" "	0·171		"	5·5	Bn.
" "	0·178		"	5·7	Rg.
<sup>6</sup> Potassium	0·166	- 78° to + 10°	39·04	6·5	Rg.
Calcium	0·170		39·9	6·8	Bn.
<sup>6</sup> Chromium	0·10		52·4	5·2	Kp.
<sup>7</sup> Manganese	0·122		55	6·7	Rg.
Iron	0·112		55·9	6·3	Kp.
"	0·114		"	6·4	Rg.
"	0·110		"	6·1	D.P.
Nickel	0·108		58·6	6·3	Rg.
Cobalt	0·107		59	6·3	Rg.
Copper	0·093		63·4	6·0	Kp.
"	0·095		"	6·1	Rg.
"	0·095		"	6·1	D.P.
Zinc	0·0932		64·9	6·1	Kp.
"	0·0935		"	6·1	Bn.
"	0·0955		"	6·2	Rg.
"	0·093		"	6·0	D.P.
<sup>8</sup> Gallium	0·079	12° to 23°	69	5·4	Bt.
Arsenic—amorphous	0·076†		74·9	5·7	B.W.
" crystalline	0·083†		"	6·2	B.W.

<sup>1</sup> *Annalen, Supplbd. 3. 1 and 189.*

<sup>2</sup> When no temperature is given the determinations were made somewhere between the limits 0° and 100°: the numbers may in these cases be regarded as the mean specific heats at 40°—60°.

Name	Spec. heat	Temp.	Atomic weight	Sp. ht. x at. wt.	Observer
Arsenic—crystalline	0'0814		74'9	6'1	Rg.
"	0'0822		"	6'2	N.
<sup>9</sup> Selenion—amorphous	0'0746	-27° to +8°	78'8	5'9	Rg.
" crystalline	0'0745	-18° to +7°	"	5'9	Rg.
"	0'0762		"	6'0	Rg.
"	0'0861		"	6'8	N.
"	0'084†		"	6'7	B.W.
Bromine—solid	0'0843	-78° to -20°	79'75	6'7	Rg.
<sup>10</sup> Zirconium	0'0666		90'0	6'0	M.D.
<sup>11</sup> Molybdenum	0'0722		95'8	6'9	Rg.
Rhodium	0'058		104	6'0	Rg.
Ruthenium	0'0611		104'5	6'4	Bn.
Palladium	0'0593		106'2	6'3	Rg.
Silver	0'056		107'66	6'0	Kp.
"	0'0559		"	6'0	Bn.
"	0'057		"	6'1	Rg.
Cadmium	0'0542		112	6'0	Kp.
"	0'0548		"	6'1	Bn.
"	0'0567		"	6'3	Rg.
Indium	0'057		113'4	6'5	Bn.
Tin	0'0548		117'8	6'5	Kp.
"	0'0559		"	6'6	Bn.
"	0'0562		"	6'6	Rg.
"	0'0514		"	6'0	D.P.
Antimony	0'0523		120'0	6'2	Kp.
"	0'0495		"	5'9	Bn.
"	0'0508		"	6'0	Rg.
"	0'0507		"	6'0	D.P.
Iodine	0'0541		126'53	6'8	Rg.
Tellurium	0'0475		127'5	6'0	Kp.
"	0'0474		"	6'0	Rg.
Lanthanum	0'0449		138'5	6'2	Hd.
Cerium	0'0448		141	6'3	Hd.
Didymium	0'0456		144	6'5	Hd.
Tungsten	0'0334		183'6	6'0	Rg.
Osmium	0'0311		193	6'0	Rg.
Iridium	0'0326		194	6'2	Rg.
Platinum	0'0325		195	6'4	Kp.
"	0'0324		"	6'3	Rg.
"	0'0314		"	6'3	D.P.
<sup>12</sup> Gold	0'0324		196'2	6'0	Rg.
<sup>13</sup> Mercury—solid	0'0319	-78° to -40°	199'8	6'4	Rg.
<sup>14</sup> Thallium	0'0335		203'6	6'8	Rg.
Lead	0'0307		206'4	6'3	Rg.
"	0'0315		"	6'5	Kp.
"	0'0314		"	6'5	Rg.
Bismuth	0'0305		208	6'3	Kp.
"	0'0308		"	6'3	Rg.
Thorium	0'0276		232'4	6'4	Nn.
Uranium	0'028		240	6'6	Zn.

*Notes to preceding Table.*

<sup>1</sup> The number for beryllium is that calculated by L. Meyer from the data of Nilson and Pettersson: for fuller discussion of specific heat of beryllium see par. 28, pp. 58, 59.

<sup>2,3,4</sup> Spec. heats of boron, carbon and silicon are discussed on pp. 59—61, par. 29.

<sup>5</sup> The higher temperature ( $+10^{\circ}$ ) is not given in Regnault's paper, but judging from the context it appears to be approximately correct.

<sup>6</sup> This number for chromium is probably too low; see Kopp, *Annalen*, **Supplbd.** 3. 77 (note).

<sup>7</sup> The specimen of manganese employed contained a little silicon.

<sup>8</sup> Spec. heat of molten gallium between  $109^{\circ}$  and  $119^{\circ}=0.802$ . (Berthelot, *Bull. Soc. Chim.* 31. 229.)

<sup>9</sup> Spec. heat of amorphous selenium determined at high temperatures is abnormal, because of large quantity of heat absorbed before fusion.

<sup>10</sup> Spec. heat of zirconium calculated by Mixter and Dana from determinations made with sample containing known quantities of aluminium.

<sup>11</sup> The specimen of molybdenum employed contained carbon.

<sup>12</sup> Spec. heat of gold is nearly constant from  $0^{\circ}$  to  $600^{\circ}$ ; at  $900^{\circ}$  sp. ht. =  $0.345$ ; and at  $1000^{\circ}=0.352$ . [Violle, *Compt. rend.* 89. 702.]

<sup>13</sup> Spec. heat of liquid mercury at  $55^{\circ}=0.33$  (Regnault).

<sup>14</sup> The specimen of thallium employed contained a little oxide.

The numbers marked with ‡ are probably too large; see Weber's papers referred to below.

The names of the various observers are abbreviated in the table:

RG. stands for REGNAULT,—his papers on spec. heat are to be found in						{ <i>Ann. Chim. Phys.</i> [2] 73. 5: [3] 1. 129: 9. 322: 26. 261: 38. 129: 46. 257: 63. 5: and 67. 427.
KP.	„ „	KOPP,	„ „ „	„ „ „	<i>Annalen</i> 126. 362: and <i>Supplbd.</i> 3. 1 and 289.	
N.	„ „	NEUMANN,	„ „ „	„ „ „	<i>Pogg. Ann.</i> 126. 123.	
BN.	„ „	BUNSEN,	„ „ „	„ „ „	<i>Pogg. Ann.</i> 141. 1.	
WB.	„ „	WEBER,	„ „ „	„ „ „	<i>Pogg. Ann.</i> 154. 367 [trans- lation in <i>Phil. Mag.</i> (4) 49. 161 and 276.]	
D. P.	„ „	DULONG and PETIT,	„ „ „	„ „ „	<i>Ann. Chim. Phys.</i> 10. 395.	
BT.	„ „	BERTHELOT,	„ „ „	„ „ „	<i>Compt. rend.</i> 86. 786.	
HD.	„ „	HILLEBRAND,	„ „ „	„ „ „	<i>Pogg. Ann.</i> 163. 71 [trans- lation in <i>Phil. Mag.</i> (5) 3. 109].	
B. W.	„ „	BETTENDORF and WULLNER	„ „ „	„ „ „	<i>Pogg. Ann.</i> 133. 293.	
M. D.	„ „	MIXTER and DANA,	„ „ „	„ „ „	<i>Annalen</i> , 169. 388.	
NN.	„ „	NILSON,	„ „ „	„ „ „	<i>Ber.</i> 15. 2519.	
MT.	„ „	MALLET,	„ „ „	„ „ „	<i>Chem. News</i> , 46. 178.	
ZN.	„ „	ZIMMERMANN,	„ „ „	„ „ „	<i>Ber.</i> 15. 849.	

26. The preceding table contains the names of 49 elements, the specific heats of which have been directly determined. For eleven of the remaining elements values have been obtained which are regarded by some chemists as representing the specific heats of these elements: the method employed is based on the assumption that the *molecular heat*<sup>1</sup> of a solid compound is equal to the sum of the atomic heats of its constituent elements. (See Kopp, *Annalen*, **Suppl.** 3. 321—339.) Thus Kopp found the mean *molecular heat*<sup>1</sup> of metallic sulphides of the form RS to be equal to 12: the atomic heat of sulphur is 5·7; but  $12 - 5·7 = 6·5$ , which number is regarded as the value of the atomic heat of any one of the metals R. The mean value of the atomic heats of these metals found by direct experiment is 6·4.

Kopp has applied this indirect method to calculate the atomic heats of various elements with which direct experiments could not be made<sup>2</sup>.

*Chlorine*: molecular heats of metallic haloid salts:—

$$\begin{aligned} \text{RCl} &= 12·8 & \text{RBr} &= 13·9 & \text{RI} &= 13·4 \\ \text{RCl}_2 &= 18·5 & \dots\dots\dots & & \text{RI}_2 &= 19·4. \end{aligned}$$

Now as (1) the atomic heat of each of the metals R is about 6·4; (2) the atomic heat of solid bromine and iodine is about 6·6; (3) the chlorides, bromides and iodides examined are chemically analogous; and (4) the molecular heats of the analogous salts are nearly the same, Kopp concludes that the atomic heat of solid chlorine is about 6·4.

$$\text{RCl } (12·8) - \text{R } (6·4) = 6·4 : \text{RCl}_2 \text{ } (18·5) - \text{R } (6·4) = 12·1, \text{ and } \frac{12·1}{2} = 6·05.$$

A further argument in favour of this conclusion is afforded by these data,

$$\begin{aligned} &\text{molecular heat of KClO}_3 = 24·8 \\ &\text{„ „ KAsO}_3 = 25·3, \end{aligned}$$

hence the atomic heats of arsenic and chlorine are probably

<sup>1</sup> By *molecular heat* is to be understood the product obtained by multiplying the specific heat of a compound into the quantity expressed by the generally accepted formula of that compound; the expression *formula-weight* will be employed to signify this amount of any compound.

<sup>2</sup> For detailed data see Kopp, *loc. cit.* p. 293.

nearly the same ; but the atomic heat of arsenic is 6·1, therefore the atomic heat of solid chlorine is probably about 6·1.

*Fluorine :*

molecular heat of  $\text{CaF}_2 = 16\cdot4$

atomic heat of Ca = 6·8,

hence atomic heat of fluorine =  $\frac{16\cdot4 - 6\cdot8}{2} = 4\cdot8$ .

*Nitrogen :* molecular heats of various more or less analogous compounds :—

$\text{RClO}_3 = 24\cdot8$

$\text{RCO}_3 = 20\cdot7$

$\text{RAsO}_3 = 25\cdot3$

$\text{RSiO}_3 = 20\cdot5$

$\text{RPO}_3 = 22\cdot1$

$\text{RNO}_3 = 23\cdot0$ .

Hence, it is argued, the atomic heat of solid nitrogen is probably rather less than that of chlorine or arsenic (about 6), somewhat greater than that of carbon or silicon (about 5·2), and nearly equal to that of phosphorus (about 5·8); therefore the value of the atomic heat of solid nitrogen probably lies between 5·5 and 5·8.

*Oxygen :* the molecular heats of metallic oxides are, as a rule, rather less than those of corresponding haloid salts ; therefore the atomic heat of solid oxygen is probably less than 6 ; thus

$\text{RO} = 11\cdot1 \dots \text{RCl} = 12\cdot8 \quad \text{RBr} = 13\cdot9 \quad \text{RI} = 13\cdot4,$

$\text{RO}_2 = 13\cdot7 \dots \text{RCl}_2 = 18\cdot6 \dots \text{RI}_2 = 19\cdot4$

Further data for finding the value sought for are these,

molecular heats..... $\text{R}_2\text{O}_3 = 27\cdot2$  ;  $\text{KAsO}_3 = 25\cdot3$  ;  $\text{KClO}_4 = 26\cdot3$  ;

$\text{KMnO}_4 = 28\cdot3$ .

The values deduced for the atomic heat of solid oxygen are,

from  $\text{RO} \dots 4\cdot6$ , from  $\text{KAsO}_3 \dots 4\cdot2$

„  $\text{RO}_2 \dots 3\cdot7$ , „  $\text{KClO}_4 \dots 3\cdot5$  [assuming  $\text{Cl} = 6$ ]

„  $\text{R}_2\text{O}_3 \dots 4\cdot8$ , „  $\text{KMnO}_4 \dots 3\cdot8$ ,

hence the mean value is 4·1.

*Hydrogen :* the principal data are these,

molecular heat of ice ( $\text{H}_2\text{O}$ ) = 9 : molecular heat of  $\text{Cu}_2\text{O} = 15\cdot6$ .

Hence, it is argued, the atomic heat of solid hydrogen is probably less than that of copper by the amount  $\frac{15\cdot6 - 9}{2} = 3\cdot3$  :

but atomic heat of copper = 6·4, therefore the atomic heat of solid hydrogen = 3·1.

Molecular heat of  $\text{NH}_4\text{Cl}$  = 20 : {but atomic heat of  $\text{N}^1$  is about 5·6  
and "  $\text{Cl}^1$  " 6·4}

Now  $20 - 12 = 8$ , and  $\frac{8}{4} = 2$ , therefore the atomic heat of hydrogen is about 2.

Molecular heat of  $\text{NH}_4\text{NO}_3$  = 36·4  
" oxides  $\text{R}_2\text{O}_3$  = 27·2

Hence  $36·4 - 27·2 = 9·2$ , and  $\frac{9·2}{4} = 2·3$ .

The mean of these three results is 2·4, which may perhaps be taken to represent the atomic heat of solid hydrogen: the method of calculation however involves many assumptions and the use of numbers themselves obtained by indirect means. From experiments with palladium charged with hydrogen, Beketoff deduced the number 5·9 as representing the atomic heat of solid hydrogen<sup>2</sup>.

The molecular heats of the oxides, chlorides, carbonates, nitrates, and sulphates of *calcium*, *barium*, and *strontium* are nearly the same as the molecular heats of the corresponding salts of metals the atomic heats of which have been directly determined, and found to be represented by the mean number 6·4; hence the atomic heats of *calcium*, *barium*, and *strontium* are probably represented by a number approximately equal to 6·4.

The agreement noticed between the values of the molecular heats of the chloride and carbonate of *rubidium*, of the oxides and chlorides of *chromium* and *titanium*, and of the oxides of *vanadium* and *zirconium*, and the molecular heats of corresponding salts of other metals which themselves exhibit the mean atomic heat 6·4, shews that the atomic heat of *rubidium*, *titanium*, *zirconium*, *chromium* and *vanadium* is probably about 6·4<sup>3</sup> (see notes 6 and 10 to table of specific heats of elements, p. 50).

<sup>1</sup> Indirectly determined, see p. 51 and p. 52.

<sup>2</sup> See abstract of Beketoff's paper (original is in Russian) in *Ber.* 12. 687.

<sup>3</sup> For a full collection of specific heat data see F. W. Clarke's *Constants of Nature*, part II: or, Landolt and Börnstein's *Physikalisch-chemische Tabellen*.



The following numbers representing molecular heats of salts of recently discovered elements are given by Nilson (*Ber.* 13. 1459 *et seq.*).

		Specific heat.	Temperature.	Molecular heat.
<i>Scandium salts</i> (Sc=44·03)	Sc <sub>2</sub> O <sub>3</sub>	0·153	0° – 100°	20·81
	Sc <sub>2</sub> ·3SO <sub>4</sub>	0·1639	"	62·42
<i>Erbium salts</i> (Er=166)	Er <sub>2</sub> O <sub>3</sub>	0·065	"	24·7
	Er <sub>2</sub> ·3SO <sub>4</sub>	0·104	"	64·5
<i>Yttrium salts</i> (Y=89·5)	Y <sub>2</sub> O <sub>3</sub>	0·1026	"	23·3
	Y <sub>2</sub> ·3SO <sub>4</sub>	0·1319	"	61·6
<i>Ytterbium salts</i> (Yb=173)	Yb <sub>2</sub> O <sub>3</sub>	0·0646	"	25·5
	Yb <sub>2</sub> ·3SO <sub>4</sub>	0·104	"	65·8
<hr/>				
<i>Gallium oxide</i>	Ga <sub>2</sub> O <sub>3</sub>	0·1062	"	19·5
<i>Indium oxide</i>	In <sub>2</sub> O <sub>3</sub>	0·0807	"	22·2

If we assume that the atomic heat of oxygen is 4·1 (see p. 52), and regard only the oxides in the above table, then the following values are found for the atomic heats of the metals,

$$\text{Sc}=4\cdot2 \quad \text{Er}=6\cdot1 \quad \text{Y}=5\cdot5 \quad \text{Yb}=6\cdot6 : \quad \text{Ga}=3\cdot6 \quad \text{In}=5\cdot0.$$

If a similar process is applied to the sulphates (atomic heat of S=6), then the atomic heats of the metals are all represented by negative numbers; hence either (1) the value of the atomic heat of oxygen in compounds is not constant, or (2) that of sulphur varies, or (3) that of the metals Sc, Er, Y, Yb, Ga, In, is negative in their sulphates, and, for some of these metals, is abnormal in their oxides.

The last hypothesis can scarcely be adopted. Indeed if the atomic heats of gallium and indium as determined by direct experiment are placed beside the numbers obtained by calculation from the molecular heats of the oxides (assuming O = 4·1) we have this result :

	Directly determined.	Calculated from oxides.
Atomic heat of Gallium	5·4	3·6
" Indium	6·5	5·0

We can scarcely hesitate which numbers to prefer.

It seems then that the value to be assigned to the atomic

heat of oxygen in oxides<sup>1</sup> (and probably also the value of the atomic heat of sulphur in sulphates) is not a constant number, but varies according to the metal with which the oxygen is combined<sup>2</sup>: but if this is so, much doubt must necessarily be thrown on the accuracy of the conclusions regarding the atomic heats of chlorine, nitrogen, and other elements, deduced from the molecular heats of compounds of these elements. It appears then that the Garnier-Cannizzaro generalisation (see *ante*, p. 47) cannot always be applied.

Although a knowledge of the molecular heats (so-called) of solid compounds may give considerable help towards fixing the formulæ of these compounds, and so, indirectly, deciding what multiple of the combining number of an element is to be adopted as the atomic weight of that element, yet, it appears to me, that so far as concerns the direct determination of atomic weights, only those values for specific heats which have been obtained by experiments on the solid elements themselves are of much value.

It is certain that in some cases quite erroneous conclusions regarding the value of an atomic weight may be deduced from measurements of the specific heats of solid compounds. Thus it was for some time doubtful whether the value 120 or 240 should be assigned to the atomic weight of uranium. In 1878 Donath found the specific heat of uranoso-uranic oxide to be 0.0798 (*Ber.* 12. 742); assuming the specific heat of solid oxygen to be 0.25 (i.e.  $\frac{4.1}{16}$ ), the specific heat of uranium was calculated to be 0.0497; now  $0.0497 \times 120 = 5.96$ , therefore it was concluded by Donath that the atomic weight of uranium is 120. But in 1880—I pure uranium was prepared by Zimmermann (for details see *Ber.* 14. 440 and 779: 15. 849), and the specific heat of this metal was found by him

<sup>1</sup> Such phrases as 'atomic heat of oxygen in oxides,' 'atomic heat of sulphur in sulphates' are perhaps rather misleading; they seem to assume that an elementary atom has different capacities for heat according to the nature (and number) of other atoms with which it is combined, and that measurements of these various capacities are obtainable; this assumption is not, I think, fully justified by facts.

<sup>2</sup> See *post*, chapter III. par. 111.

to be '028; but  $'028 \times 120 = 3.3$ : hence, to bring the atomic heat of uranium into agreement with that of the majority of the elements it is necessary to assign to the atomic weight of this metal the value 240.

27. If the table of maximum atomic weights (p. 45) is compared with that which gives the specific heats of elements (pp. 48—49), it will be found—omitting the four elements which are placed in brackets in the former table—that of the 34 elements whose atomic weights have been determined by the application of Avogadro's law, 24 have also had values assigned to their specific heats by direct experiments. Comparing the products obtained by multiplying the atomic weight into the specific heat in each of these 24 cases, it is found that 4 of those products fall below 5.8 (varying from 5.7 to 5.2), and that 20 vary from 6.8 to 6, giving a mean value of 6.4, round which number most of the values are grouped. The conclusion to be drawn is that the atomic heat of the 20 elements in question is represented by the number 6.4. There are four elements in brackets in the table on p. 45, viz. aluminium, iron, copper, and gallium: if the maximum atomic weight of each, as deduced by Avogadro's law, is multiplied into the specific heat of the element, the product is found to be about 12, but if the true atomic weights are assumed to be half as large as the numbers in the table, then the atomic heat of each of these elements is represented by the mean number 6.4. Now there are no valid reasons against adopting half the maximum values obtained by Avogadro's law as the true values of the atomic weights of the four elements in question, indeed there are strong chemical reasons in favour of this course.

Hence we have a very considerable mass of facts in favour of the generalisation,—

*The atomic heat of all solid elements is nearly a constant, the mean value being 6.4.*

If this be granted, we deduce the statement for finding the atomic weight of an element,—

$$\text{atomic weight} = \frac{6.4}{\text{spec. heat}},$$

provided always it is remembered that the specific heat is assumed to be determined with the element in the solid form, and for a considerable range of temperature; and also that the quotient  $\frac{6.4}{\text{sp. ht.}}$  affords only an approximate value for the atomic weight of the element.

This method for determining the atomic weights of elements has been applied in about 20 cases, besides those cases where the method of specific gravities has also been employed; the numbers obtained are usually regarded as the true atomic weights of the elements in question.

It is evident that in determinations of the specific heats of solid elements we have a most valuable means for deciding which multiple of the combining number of an element is to be accepted as most probably expressing the value of the atomic weight of that element. When the element cannot be obtained, or cannot be obtained in sufficient quantity in the solid form, then measurements of the specific heats of a series of its solid compounds will afford more or less valuable guidance in attempts to find the atomic weight of the element in question.

The following statement fairly sums up the results of atomic heat determinations.

I. *Solid elements, forty-four in number, whose specific heats have been directly determined, and whose atomic heats are all nearly equal to 6.4.*

Li Na Mg Al P S K Ca Mn Fe Co Ni Cu Zn As  
Se Br Zr Mo Ru Rh Pd Ag Cd In Sn Sb I Te La  
Ce Di W Os Ir Pt Au Hg Tl Pb Bi Th U.....(Cr)

II. *Solid elements, five in number, whose specific heats have been directly determined, and whose atomic heats appear to be about 5.5.*

Ga [? inaccurately determined] Be B C Si.

III. *Solid elements, six in number, whose specific heats have been indirectly determined, and whose atomic heats are probably nearly equal to 6.4.*

Ca Ti V Rb Sr Ba.

IV. *Gaseous elements; atomic heats very doubtful, apparently variable.*

H (F) N O CL

Of the elements whose atomic heats are decidedly less than 6·4, all, except gallium and beryllium, are nonmetallic and have atomic weights smaller than 33: indeed if the elements are arranged in order of increasing atomic weight, it is found that, with the exception of lithium, all having an atomic weight less than 23 have also an atomic heat less than 6, and that these elements, except beryllium, are nonmetallic.

28. The data concerning specific heats of beryllium, boron, carbon, and silicon must be examined in some detail.

*Beryllium.* R. E. Reynolds (*Phil. Mag.* (5) 3. 38) determined the specific heat of this metal at 100° to be 642: the metal used was however impure.

Nilson and Pettersson (*Ber.* 11. 351) determined the specific heat of a mixture of metallic beryllium with known quantities of beryllium oxide, ferric oxide and silica; they also determined the specific heat of pure beryllium oxide, and, the specific heats of ferric oxide and silica being known, they calculated the specific heat of the metal beryllium to be 4079, for the temperature interval 0° – 100°.

The same chemists (*Ber.* 13. 1451: see also *Chem. News*, 42. 297) made a second series of determinations with a sample of the metal containing only about 5 per cent. of beryllium and ferric oxides. The following table gives their more important results:

*Specific heat of Beryllium.* (NILSON and PETERSSON.)

Temperature interval.	Specific heat.	Sp. ht. $\times 13\cdot65$ .
0°–46·5°	0·3973	5·4
0°–100°	0·4246	5·8
0°–214°	0·475	6·4
0°–300°	0·5055	6·9

Hence these chemists concluded that the atomic weight of beryllium ought to be taken as 13·65, and not 9·1 the value usually assigned to this constant.

The results tabulated above show that the value of the specific heat of beryllium for the interval  $0^{\circ}$ — $300^{\circ}$  is

27 per cent. greater than the value for the interval  $0^{\circ}$ — $50^{\circ}$ ; is

7 " " "  $0^{\circ}$ — $200^{\circ}$ ; and is  
19 " " "  $0^{\circ}$ — $100^{\circ}$ .

Using the data of Nilson and Pettersson, L. Meyer (*Ber.* 13. 1780), has calculated the values of the specific heat of beryllium at various temperatures, with the following results.

*True specific heat of Beryllium at various temperatures.* (MEYER.)

$\gamma$  = true specific heat at temperature  $t$ .

$\Delta\gamma$  = increase in value of  $\gamma$  per  $1^{\circ}\text{C}$ .

$t$ .	$\gamma$ .	$\Delta\gamma$ .	Atomic heat	
			$Be = 9.1$	$Be = 13.65$
$20.2^{\circ}$	0.3973	0.00101	3.62	5.43
$73.2^{\circ}$	0.4481	0.00085	4.08	6.12
$157^{\circ}$	0.5193	0.00063	4.73	7.10
$256.8^{\circ}$	0.5819	—	5.29	8.94

Hence it appears that the specific heat of beryllium increases rapidly as temperature increases, but that the rate of this increase diminishes: the specific heat probably attains a constant value, equal to about 0.6, at  $300^{\circ}$  or so<sup>1</sup>.

29. *Boron, Carbon, and Silicon.* Very varying values have been obtained for the specific heats of these three elements. The following table summarises the principal data previous to the publication of Weber's papers [see *Phil. Mag.* (4) 49. 161 & 276].

*Specific heats of Boron, Carbon, Silicon.* (Weber's numbers not included.)

(Temperature may be taken as about  $35^{\circ}$ — $55^{\circ}$ .)

	Sp. ht.	Sp. ht. $\times$ at. wt.	Observer.	
Boron—amorphous	0.254	2.8	Kp.	1864
" crystalline	0.230	2.6	"	"
" "	0.252	2.8	M.D.	1873
" "	0.262	2.9	Rg.	1869

<sup>1</sup> For a discussion of the value to be assigned to the atomic weight of beryllium see chapter III. par. 111.

	Sp. ht.	Sp. ht. x at. wt.	Observer.	
Boron—crystalline	0'225	2'5	Rg.	1869
" "	0'257	2'8	"	"
" graphitic	0'235	2'6	"	"
<sup>1</sup> Carbon—diamond	0'143	1'7	B.W.	1868
" "	0'147	1'8	Rg.	1841
" gas-carbon	0'165	2'0	Kp.	1864
" "	0'186	2'2	B.W.	1868
" "	0'197	2'4	Rg.	1841
" graphite	0'174	2'1	Kp.	1864
" "	0'188	2'3	B.W.	1868
" "	0'198	2'4	Rg.	1866
Silicon—fused	0'138	3'9	Kp.	1864
" "	0'166	4'6	Rg.	1861
" crystalline	0'165	4'6	Kp.	1864
" "	0'171	4'8	M.D.	1873
" "	0'173	4'8	Rg.	1861

Weber (*loc. cit.*) found that the specific heats of carbon, boron, and silicon increase rapidly as the temperature is raised, but that at high temperatures the velocity of the increase becomes much smaller. The following table gives a synopsis of Weber's results :

*Specific heats of Boron, Carbon, and Silicon. (WEBER.)*

	Temp.	Spec. heat.	Spec. ht. x at. wt.
Boron—crystallised	- 40°	0'1915	2'11
" "	+ 77°	0'2737	3'01
" "	177°	0'3378	3'72
" "	233°	0'3663	4'03

These numbers show that the specific heat of boron increases with increase of temperature, and that the value of this increase, for a given interval, is considerably less at high than at low temperatures. The variations in the rate of this increase are almost identical with the variations noticed in the case of carbon ; hence at temperatures above 233°

<sup>1</sup> Dewar (*Phil. Mag.* [4] 44. 461) found for the specific heat of gas-carbon between 20° and 1040° the number 0'32, for diamond the number 0'366; and between 20° and a temperature estimated to be 2000°, for 'carbon' the number 0'42.

this identity will probably remain. Calculated on this assumption, the specific heat of boron at about  $1000^{\circ}$  is  $0\cdot50$ .

*Specific heats of Boron, Carbon, and Silicon.* (WEBER) continued.

	Temp.	Spec. heat.	Sp. ht. x at. wt.
Carbon—diamond	$-50^{\circ}$	$0\cdot0635$	$0\cdot76$
" "	$+10^{\circ}$	$0\cdot1128$	$1\cdot35$
" "	$85^{\circ}$	$0\cdot1765$	$2\cdot12$
" "	$250^{\circ}$	$0\cdot3026$	$3\cdot63$
" "	$606^{\circ}$	$0\cdot4408$	$5\cdot29$
" "	$985^{\circ}$	$0\cdot4589$	$5\cdot51$
" graphite	$-50^{\circ}$	$0\cdot1138$	$1\cdot37$
" "	$+10^{\circ}$	$0\cdot1604$	$1\cdot93$
" "	$61^{\circ}$	$0\cdot1990$	$2\cdot39$
" "	$201^{\circ}$	$0\cdot2966$	$3\cdot56$
" "	$250^{\circ}$	$0\cdot325$	$3\cdot88$
" "	$641^{\circ}$	$0\cdot4454$	$5\cdot35$
" "	$978^{\circ}$	$0\cdot467$	$5\cdot50$
Porous wood carbon	$0^{\circ}-23^{\circ}$	$0\cdot1653$	$1\cdot95$
"	$0^{\circ}-99^{\circ}$	$0\cdot1935$	$2\cdot07$
"	$0^{\circ}-223^{\circ}$	$0\cdot2385$	$2\cdot84$

These numbers show that the specific heat of carbon increases from  $-50^{\circ}$  upwards, the value found at  $600^{\circ}$  being about seven times as great as that found at  $-50^{\circ}$ ; but that the rate of this increase is very small at high temperatures,—from a red heat upwards the rate is about one-seventeenth of that from  $0^{\circ}$  to  $100^{\circ}$ .

The specific heats of diamond and graphite differ at temperatures below about  $600^{\circ}$ , but from this point upwards they are practically identical; the numbers given for porous wood carbon are almost the same as those for graphite at the same temperature-intervals, hence it may be said that at high temperatures (above  $600^{\circ}$ ) the various modifications of carbon have probably all the same specific heat.

*Table continued.*

	Temp.	Spec. heat.	Sp. ht. x at. wt.
Silicon—crystallised	$-40^{\circ}$	$0\cdot136$	$3\cdot81$
" "	$+57^{\circ}$	$0\cdot1833$	$5\cdot13$
" "	$128^{\circ}$	$0\cdot196$	$5\cdot50$
" "	$184^{\circ}$	$0\cdot2011$	$5\cdot63$
" "	$232^{\circ}$	$0\cdot2029$	$5\cdot68$



The specific heat of silicon attains an almost constant value at about 200°.

30. It is evident that the specific heat of an elementary body is not a constant number, but varies with the temperature, and that the relation between the variation of specific heat and that of temperature differs for each element. The following formulæ calculated from experimentally determined numbers, express the relation in question for some of the elements.

<sup>1</sup> Carbon—diamond sp. ht. =  $0.4408 + 0.0000405 t$ , where  $t$  varies from

				600°—800°
"	"	"	= $0.4408 + 0.0000561 t$	" 800°—1000°
"	graphite	"	= $0.4454 + 0.0000472 t$	" 600°—800°
"	"	"	= $0.4454 + 0.0000840 t$	" 800°—1000°
<sup>2</sup> Copper	"	"	= $0.0910 + 0.000023 t$	" 0°—250°
<sup>2</sup> Zinc	"	"	= $0.0865 + 0.000044 t$	" "
<sup>2</sup> Lead	"	"	= $0.0286 + 0.000019 t$	" "
<sup>3</sup> Platinum	"	"	= $0.0317 + 0.000006 t$	" 0°—1200°
<sup>3</sup> Iridium	"	"	= $0.0317 + 0.000006 t$	" "
<sup>2</sup> Iron	"	"	= $0.1053 + 0.000071 t$	" 0°—250°
<sup>2</sup> Tin	"	"	= $0.050 + 0.000044 t$	" "
<sup>2</sup> Antimony	"	"	= $0.0466 + 0.000020 t$	" "
<sup>2</sup> Bismuth	"	"	= $0.0269 + 0.000020 t$	" "

The specific heat of any substance also varies with variations in the physical state of that substance—thus :

	Sp. heat.		Sp. heat.
Bromine—solid ...	0.0843	Mercury— <sup>4</sup> gaseous ...	0.015
" liquid ...	0.1110	Soft steel ...	0.1165
Soft copper ...	0.0948	Hard steel ...	0.1175
Hard copper ...	0.0934	Titanium oxide as rutile ...	0.1666
Iron sulphide as strahlite	0.1332	" brookite	0.1610
" pyrites ...	0.1279	" artificial ...	0.1716
Chlorine—solid ...	0.180	Calcium carbonate as calc-	
" <sup>4</sup> gaseous ...	0.093	spar ...	0.205
Mercury—solid ...	0.032	" as arragonite	0.204

The specific heats of the elementary bodies have generally been determined at temperatures situated at very varying

<sup>1</sup> Weber (*loc. cit.*).

<sup>2</sup> Bède, *Mém. Couronn. de l'Acad. Brux.* 27. 3 (1855).

<sup>3</sup> Violle, *Compt. rend.* 85. 543.

<sup>4</sup> Calculated for constant volume.

intervals from the melting points of these elements; the physical aggregation of the specimens examined has also varied much; hence the values found for the specific heats of the elements cannot be regarded as strictly comparable.

There appears to be a certain interval of temperature within which the value of the specific heat of an element becomes nearly constant, and for this interval only can the element be said approximately to obey the law of Dulong and Petit, as stated on p. 56. This temperature-interval varies for each element, especially for the nonmetallic elements with small atomic weights; for many elements it may be roughly taken as from  $0^{\circ}$  to  $100^{\circ}$ .

Kopp (*loc. cit.*) has supposed that the atoms of certain elements—more especially of boron, carbon and silicon—are built up of simpler parts, have themselves a grained structure, and that at high temperatures the atoms of these elements are composed of a smaller number of those little parts than at lower temperatures. Heat added at low temperatures is supposed, on this hypothesis, to be used in separating the atomic groups. Kopp's hypothesis will be again referred to in the chapter on the nature of the elements; meanwhile it may be observed, that the facts of spectroscopy seem to point to the existence of a more complex structure in the nonmetallic than in the metallic molecules; that allotropy occurs markedly only among the nonmetals; that the molecules of the two metallic elements whose vapour-densities have been determined are monatomic; that the atomic heat of tellurium, a metal-like nonmetal belonging to the oxygen group, is 6.0, of the less metal-like selenion about 5.8, of the decidedly nonmetallic sulphur about 5.5, and of the typical nonmetal oxygen probably not more than 4; and finally that the molecular structures of oxygen, sulphur, and selenion vapours are more complex than that of tellurium vapour.

31. A consideration of the data which has been summarised in the preceding paragraphs shews, I think, that the application of Avogadro's law is of more value to the chemist as a means of determining the atomic weights of elements,

than the law of Dulong and Petit. From a general consideration of the molecular theory of matter it is also apparent that a deduction which does not necessitate an exact hypothesis as to the internal structure of molecules is more trustworthy and more appropriate, in the present state of knowledge, than another which does necessitate some such hypothesis.

The molecular explanation of the gaseous laws expressing relations between volume, pressure and temperature, and of Avogadro's law, may be considered as fairly complete; but in order to explain the law of molecular specific heats more knowledge of the internal structure of molecules than we now possess is necessary<sup>1</sup>. For the specific heat of a substance depends on the rate at which the whole energy of the molecule increases with increase of temperature: but this energy is made up of two parts, (1) the energy of agitation, that is, the energy the molecule would possess if it moved as a whole with the motion of its centre of mass, or in other words without rotation; and (2) the energy of rotation, that is, the energy the molecule would possess if its centre of mass were reduced to rest, in other words the energy due to the motion of the parts relatively to the centre of mass of the molecule<sup>2</sup>. If it is assumed that the energy due to the rotational motions of the parts of the molecule tends towards a value having a constant ratio to the energy of agitation of the molecule, then a simple-expression is found for the whole energy; but this expression contains a factor which varies in different gases, and the value of which has been determined only in a few cases<sup>3</sup>. And moreover it is probable that when the energy due to the rotational motions of the parts of a molecule becomes greater than a certain quantity, the molecule separates into parts; hence when heat is imparted to a mass of molecules work is probably in many cases done in destroying some of the molecules as such<sup>4</sup>. Hence the molecular expla-

<sup>1</sup> Clerk Maxwell, *C. S. Journal* [2] 13. 507.

<sup>2</sup> Clerk Maxwell, *loc. cit.* p. 502.

<sup>3</sup> See Clerk Maxwell's *Heat*, pp. 317—319 (6th ed.).

<sup>4</sup> See Hicks, *Phil. Mag.* (5). 4. 80, and 174. 'On some effects of Dissociation on the Physical Properties of Gases.'

nation of specific heat is not at present in so advanced a state as that of the relations between the volumes, pressures and temperatures of gases<sup>1</sup>.

32. The so-called 'law of isomorphism' affords a basis on which is founded another method for determining the atomic weights of elementary substances.

The Abbé Haüy, whose views were dominant in crystallography in the early days of this century, admitted a close connection between crystalline form and chemical composition, but he thought that each chemically distinct body must be characterised by a definite and peculiar form.

In 1816 Gay-Lussac noticed that the growth of crystals of potash alum was not affected by placing them in a solution of ammonia alum.

Various observations of this kind were made from time to time<sup>2</sup> until 1819, when E. Mitscherlich propounded the law of isomorphism, which, modified and developed, was stated by him in 1821 in the following terms: 'Equal numbers of atoms similarly combined exhibit the same crystalline form; identity of crystalline form is independent of the chemical nature of the atoms, and is conditioned only by the number and configuration of the atoms.'

Since this date various observers have advanced the knowledge of the relations between crystalline form and chemical composition<sup>3</sup>. The more important generalisations are as follows.

Similar atomic structure is not necessarily accompanied by identical crystalline form;

e.g.  $\text{PbCrO}_4$  monoclinic, and  $\text{PbMoO}_4$  quadratic;

$\text{AgCl}$  and  $\text{AgBr}$  regular, and  $\text{AgI}$  hexagonal;

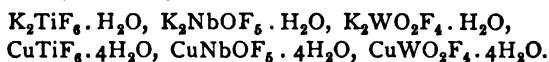
$\text{KNO}_3$  and  $(\text{NH}_4)\text{NO}_3$  rhombic but not identical,  $\text{CsNO}_3$  and  $\text{RbNO}_3$  hexagonal.

<sup>1</sup> See in connection with this subject Strecker, *Wied. Ann.* 13. 20; and Boltzmann, *do.* 13. 544: and 18. 309.

<sup>2</sup> For a full historical account of the development of the conception of *Isomorphism*, with copious references, see the article 'Isomorphie' in the *Neues Handwörterbuch der Chemie*, Bd. III. p. 844 *et seq.*

<sup>3</sup> See especially *Handwörterbuch*, *loc. cit.* and Kopp's *Lehrbuch der physikalischen und theoretischen Chemie* (2nd Ed.), Bd. II. pp. 136—155.

Unlike atomic structure may be accompanied by similar or identical crystalline form: thus Marignac<sup>1</sup> shewed that the following salts crystallise in identical forms;—



In these salts we must suppose isomorphism to occur between certain groups, e.g.  $\text{TiF}_6$ ,  $\text{NbOF}_6$ , and  $\text{WO}_4$ . The isomorphism of potassium and ammonium salts shews that the atom K is crystallographically equivalent to the group of atoms  $\text{NH}_4$ .

The form of the constituents of isomorphous compounds cannot always be deduced from that of the compounds themselves; e.g. manganous and manganic sulphides crystallise in regular, but sulphur in rhombic or monoclinic forms, therefore manganese does not necessarily crystallise in regular forms. So also the sulphates of nickel, magnesium and zinc crystallise in rhombic forms, but the oxides of nickel and magnesium in regular, and oxide of zinc in hexagonal forms. Again, arsenic usually crystallises in rhombic forms, the crystals of phosphorus belong to the regular system, yet the analogous compounds of these elements are generally isomorphous. Kopp generalises such facts as these in the following statement:—‘Bodies possessing the same crystalline form combine ‘in fixed proportions to form crystals whose form is independent of, and often different from, that of their constituents.’

In other cases the constituents of isomorphous bodies are themselves isomorphous, e.g. the compound  $3\text{Ag}_2\text{S} \cdot \text{Sb}_2\text{S}_3$  has the same crystalline form as the compound  $3\text{Ag}_2\text{S} \cdot \text{As}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{As}_2\text{S}_3$  are isomorphous in rhombic forms, and arsenic and antimony form almost identical rhombic crystals. Hence we must distinguish strict isomorphism as applied to bodies which, with similar composition, exhibit the same or nearly the same crystalline form; and isomorphism as more loosely applied to bodies which, although not themselves crystallising in the same form, nevertheless combine with other bodies to produce strictly isomorphous compounds into which they enter as corresponding groups<sup>2</sup>.

<sup>1</sup> *Ann. Chim. Phys.* 60. 257.

<sup>2</sup> Kopp, *Lehrbuch*, &c. *loc. cit.*

A certain latitude is generally allowed in the application of the term 'truly isomorphous crystals.' This latitude has gradually been more and more advanced until it has become difficult to give an exact meaning to the expression. The measurements of the angles of two salts are sometimes identical<sup>1</sup>; chemically analogous compounds sometimes crystallise in forms closely resembling one another, yet belonging to different systems<sup>2</sup>; salts with identical crystalline form sometimes exhibit optical differences<sup>3</sup>. Are all such salts to be called truly isomorphous? Kopp<sup>4</sup> proposes that only those salts, any one of which is capable of growing in unmodified form when immersed in a solution of any other, should be regarded as strictly isomorphous.

It would appear that all the constituents of a compound exert an influence on the form of that substance. Isomorphism may not be exhibited in comparatively simple compounds of two elements, but may appear in more complex compounds of the same elements; e.g. many of the simpler compounds of cadmium are not isomorphous with the analogous compounds of the metals of the magnesium group (Mg, Mn, Fe, Co, Ni, Zn, Cu, Ca), but comparatively complex cadmium salts—such as  $\text{CdSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ —are generally isomorphous with the corresponding compounds of those metals. So many simple salts of sodium and potassium are not isomorphous, although their composition is similar, but the alums are isomorphous.

One may suppose that the presence of a large number of isomorphous atoms exerts a dominating influence over a smaller number of non-isomorphous atoms.

33. As we know the crystalline form of comparatively few elements<sup>5</sup>, the statement that such or such elements form an isomorphous group, generally means only that the analogous compounds of these elements are for the most part isomorphous.

<sup>1</sup> For examples see Roscoe and Schorlemmer's *Treatise*, I. 742.

<sup>2</sup> See Marignac, *Ann. Min.* [5] 9. and 15. &c.

<sup>3</sup> See Baker, *C. S. Journal Trans.* for 1879. 760.

<sup>4</sup> *Ber.* 12. 900 *et seq.*

<sup>5</sup> See, for crystalline forms of elements in free state, Watts's *Dictionary*, vol. III. p. 429.

The more important groups of isomorphous elements, as thus understood, are as follows<sup>1</sup>:

GROUP I. *Fluorine, Chlorine, Bromine, Iodine, [Cyanogen]*; in all compounds:

partially *Manganese*; in compounds of the type  $\text{RMnO}_4$ .

GROUP II. *Sulphur, Selenion*; in all compounds and as elements in monosymmetric forms:

partially *Tellurium*; in compounds of the type  $\text{R}''\text{Te}$ :

„ *Chromium, Manganese, Tellurium*; in salts of their acids belonging to type  $\text{H}_2\text{SO}_4$ :

„ *Arsenic, Antimony*; in compounds of the type  $\text{R}''\text{S}_2$ .

GROUP III. *Arsenic, Antimony, Bismuth, Tellurium*; as elements, and the three first-named in all corresponding compounds:

partially *Phosphorus and Vanadium*; in salts of their acids:

„ *Nitrogen with Phosphorus, Arsenic, Antimony*; in organic bases.

GROUP IV. *Lithium, Sodium, Potassium, Rubidium, Cesium, [Ammonium]*; in most compounds:

partially *Thallium*; in some compounds:

„ *Silver*, in some compounds (especially with *sodium*).

GROUP V. *Calcium, Strontium, Barium, Lead; Magnesium, Zinc, Manganese, Iron*; e.g. in carbonates:

partially *Nickel, Cobalt, Copper*; with *iron* in some compounds, e.g. sulphates:

„ *Lanthanum, Cerium, Didymium, Yttrium, Erbium*; with *calcium*, in compounds of type  $\text{R}''\text{O}$ :

„ *Copper, Mercury*; with *lead*, in oxy-compounds:

„ *Beryllium, Cadmium, Indium*; with *zinc*, in some compounds:

„ *Thallium*; with *lead*, in some compounds.

GROUP VI. *Aluminium, Chromium, Manganese, Iron*; in the sesquioxides  $[\text{R}_2\text{O}_3]$  and salts derived therefrom:

partially *Cerium, Uranium*; in their sesquioxides.

GROUP VII. *Copper, Silver*; in compounds of the type  $(\text{R}_2)''\text{O}$ :

partially *Gold*; with *silver*.

GROUP VIII. *Ruthenium, Rhodium, Palladium, Iridium, Platinum, Osmium*; in most compounds:

partially *Iron, Nickel, Gold*:

„ *Tin* [*? Tellurium*].

<sup>1</sup> From article 'Isomorphie' in *Neues Handwörterbuch*, loc. cit.

GROUP IX. *Carbon, Silicon, Titanium, Zirconium, Tin, Thorium*; partially in compounds of the type  $RO_2$ , and salts derived from the type  $H_2RO_3$ : *carbon with silicon* in many corresponding so-called organic compounds.

„ *Iron*; with *titanium*.

GROUP X. *Niobium, Tantalum*; in all their compounds.

GROUP XI. *Molybdenum, Tungsten*; in all their compounds: partially *Chromium*; in salts of acids of the type  $H_2RO_4$ .

34. The terms *dimorphous*, *trimorphous*, *polymorphous* were used by Mitscherlich. Many examples of the phenomena to which these names are applied are now known: thus calcium carbonate crystallises in hexagonal forms as calcspar, and in rhombic forms as arragonite: titanium oxide assumes two distinct quadratic forms, one being known as rutile the other as anatase, and also crystallises in brookite as rhombic prisms: arsenious oxide crystallises in octahedral, antimonious oxide in rhombic forms, but if amorphous arsenious oxide is heated in a sealed tube so that one part of the tube is at  $400^\circ$  and the rest below this temperature, the oxide deposited in the middle part of the tube is found to be isomorphous with rhombic antimonious oxide; the latter oxide is also known in octahedral forms, so that the isodimorphism of these two oxides is complete.

35. If it is assumed that, as a general rule, those amounts of two substances which are crystallographically equivalent have analogous atomic constitutions; and if we suppose that of two compounds exhibiting identical crystalline form the atomic weights of the elements in one are known, it is evident in what way determinations of crystalline form may aid in fixing atomic weights.

To take an example:—from determinations of the specific gravities of gaseous compounds and analyses of these compounds, the value 52.4 is assigned to the atomic weight of chromium; this number is verified by measurements of the specific heat of the same metal; the formula  $nCr_2O_3$  is hence assigned to the green oxide of chromium. But this oxide exhibits the same crystalline form as ferric oxide, hence the latter oxide should probably be represented by the formula



$n\text{Fe}_2\text{O}_3$ ; as this formula is quite in keeping with analyses it is assigned to ferric oxide. On comparing these crystallographically equivalent quantities of the two oxides it is found that  $52.4 \times 2$  parts of chromium are replaced by  $55.9 \times 2$  parts of iron, but as 52.4 has been determined to be the atomic weight of chromium it is argued that the atomic weight of iron is represented by the number 55.9. As the specific heat of iron multiplied into 55.9 gives the product 64, 55.9 is almost certainly the true atomic weight of iron. Again, the formulæ of potassium perchlorate and permanganate were at one time written  $\text{KO} \cdot \text{ClO}_7$  and  $\text{KO} \cdot \text{Mn}_7\text{O}_{17}$ . Berzelius proposed the formulæ  $\text{KO} \cdot \text{ClO}_4$  and  $\text{KO} \cdot \text{MnO}_4$ , which on the system of notation now adopted became  $\text{KClO}_4$  and  $\text{KMnO}_4$ , respectively: these formulæ represent crystallographically equivalent quantities of the two salts; if it is assumed that Cl represents the weight of the atom of chlorine (35.37), then Mn (55) probably represents the weight of the atom of manganese.

Observations of crystalline form have sometimes led the way to correct determinations of atomic weights or to changes in the received values of such weights. Thus H. Rose<sup>1</sup> gave the name of hyponiobium to a supposed allotropic form of the metal niobium; but Marignac<sup>2</sup> shewed that compounds of the hypothetical metal were identical in crystalline form with certain compounds of tin and titanium, and concluded that Rose's hyponiobium was itself isomorphous with the atomic groups  $\text{SnF}$  and  $\text{TiF}$ , and was therefore probably a compound. Further experiments shewed that the hyponiobium of Rose was really composed of niobium and oxygen in the proportions expressed by the formula  $\text{NbO}$ , provided that this group was regarded as crystallographically equivalent to  $\text{SnF}$  and  $\text{TiF}$ ; if this were admitted it followed, from the analyses of the various compounds, that one atom of tin or titanium (117.8 or 48 parts by weight respectively) was replaced by 94 parts by weight of niobium, and that this number therefore represented the weight of the atom of niobium<sup>3</sup>.

<sup>1</sup> *Pogg. Ann.* 108. 273.

<sup>2</sup> *Ann. Chim. Phys.* 60. 257.

<sup>3</sup> Marignac's conclusions were afterwards confirmed by determinations, by

The facts, of which an outline has been given, shew that until more extended and precise knowledge of the law expressing the connections between crystalline form and chemical constitution is obtained, that method for determining the atomic weights of elements which is founded on these connections can be applied only tentatively and in a limited number of cases. The method may however now be of considerable service in suggesting lines of research bearing on the problems connected with atomic weight determinations.

It appears probable that the crystalline form of a substance is connected at once with the internal structure of the molecules of the substance and with the configuration of the molecules themselves. No attempt has been made, nor can in the present state of knowledge hopefully be made in any but the broadest manner, to apply to the facts of crystallography the dynamical theory of the molecular structure of matter.

36. I have endeavoured to shew that the most trustworthy method for determining molecular and atomic weights is founded on Avogadro's law, which is itself an outcome of the application of dynamical reasoning to a physical theory. Formerly it was supposed that strictly chemical evidence must be of paramount importance in determining these quantities. Although the superior importance of Avogadro's law is now admitted, this law can only be applied to a limited number of substances, hence we are frequently obliged to have recourse to purely chemical evidence in support of this or that molecular weight. The nature of this evidence must now be shortly illustrated.

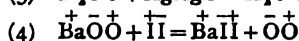
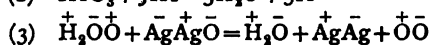
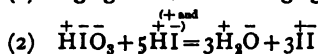
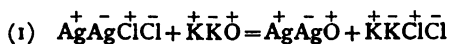
In 1850 Brodie<sup>1</sup> endeavoured to shew that there exists no difference of kind between those reactions wherein elementary bodies are produced, or react, and those in which compound bodies are alone concerned. He supposed that the small

Deville and Troost, of the specific gravity of gaseous chloride and oxychloride of niobium: see *Compt. rend.* 60. 1221.

Roscoe's researches on the atomic weight of vanadium afford a very instructive example of the employment of the results of crystallographic measurements in fixing atomic weights. *Phil. Trans.* for 1868, i. *et seq.*

<sup>1</sup> *Phil. Trans.* for 1850, 759, and also *C. S. Journal*, 4. 194.

particles of elementary substances set free during reactions, or taking part in reactions, are composed of smaller parts which exhibit certain mutual polar relations. Silver chloride is not decomposed by oxygen, but it is readily acted on by potassium oxide with production of silver oxide and potassium chloride; hydriodic and iodic acids decompose one another with production of free iodine; silver oxide decomposes hydrogen peroxide to form silver, water, and free oxygen, half of the oxygen coming from the silver oxide and half from the peroxide; iodine decomposes barium peroxide with production of barium iodide and oxygen. These reactions were thus written by Brodie (translating into the new notation):



That part of Brodie's hypothesis which supposed a polar condition of atoms in molecules was not generally adopted by other chemists, but it was admitted that his researches established a general similarity of function and composition between elementary and compound molecules.

In the same year Williamson<sup>1</sup> distinguished between the atom of zinc in combination, and the free metal zinc (that is to say, he recognised that the atom of an element is not possessed of the same properties as the molecule of that element): he said it is not quite accurate to speak of 'zinc' as existing in zinc sulphate.

Recognising then that chemical reactions took place between molecules, chemists defined the molecule as the smallest part of a substance capable of taking part in a chemical change, or as the acting chemical unit. Supposing the atomic weights of the elements forming a compound to be known, the best method of determining the molecular weight of the compound appeared to be to find that formula which should express the atomic constitution in the simplest manner.

<sup>1</sup> *C. S. Journal*, 4. 355.

Thus hydrogen and nitrogen are combined in ammonia in the proportion of 3 parts by weight of the former to 14 of the latter; assuming the atomic weights of these elements to be 1 and 14 respectively, the atomic composition of ammonia may be represented by the formula  $\text{NH}_3$ ; and as the reactions in which this substance takes part might all be represented as involving 17, or a whole multiple of 17 parts by weight of this compound, and moreover as the hydrogen in 17 parts by weight of ammonia was demonstrably divisible by chemical reactions into 3 parts, 17 was taken as the molecular weight of ammonia. An instructive illustration of this method of fixing a minimum molecular weight is furnished by Williamson's famous researches on ethers<sup>1</sup>. The formulæ generally adopted for common alcohol and ether, previous to Williamson's work, were  $\text{C}_4\text{H}_6\text{O}$ , and  $\text{C}_4\text{H}_{10}\text{O}$  respectively ( $\text{C} = 6$ ;  $\text{O} = 8$ ). Williamson allowed ethylic iodide to react on potassium alcoholate, expecting that ethylated alcohol would be produced,—thus  $\text{C}_4\text{H}_5\text{KO} + \text{C}_2\text{H}_5\text{I}$  should give  $\text{C}_4\text{H}_5(\text{C}_2\text{H}_5)\text{O} + \text{KI}$ ,—but the product was ordinary ether. If the generally accepted formula for ether were doubled the reaction would be explained, and ether would be regarded as an oxide of ethyl  $(\text{C}_2\text{H}_5)_2\text{O}$ . Again, Williamson found that when sulphuric acid acts on ethylic alcohol, and methylic alcohol is added to the mixture, a single substance having the properties of an ether, and the formula  $\text{C}_6\text{H}_{14}\text{O}$  or a whole multiple of this, distills over: if the formula of ether is  $\text{C}_4\text{H}_{10}\text{O}$ , then that of methylic ether is  $\text{C}_3\text{H}_8\text{O}$ , and a mixture of these ought to be obtained in the reaction just mentioned; but if ether is  $(\text{C}_2\text{H}_5)_2\text{O}$ , then the single ether obtained is probably methyl-ethyl oxide, i.e.  $\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)\text{O}$ , ( $= 2\text{C}_6\text{H}_{14}\text{O}$ )<sup>2</sup>. Thus was shewn, on purely chemical grounds, the necessity of doubling the generally accepted molecular formula for ether.

No purely chemical method has been found for determining molecular weights which is capable of general application; each compound must be considered as a separate

<sup>1</sup> See *C. S. Journal*, 4, 106 and 229.

<sup>2</sup> Translated into modern notation, these formulæ become  $(\text{C}_2\text{H}_5)_2\text{O}$  and  $\text{C}_3\text{H}_7(\text{CH}_3)\text{O}$  respectively.

problem. The more important methods may however be roughly classified.

There is the method of analogies, which is well illustrated by the example of ether already considered. The smallest amount of sulphuretted hydrogen which takes part in chemical changes is represented by the formula  $H_2S$  (assuming  $S = 32$ ) the hydrogen in this compound is replaceable in two parts—with production of  $KHS$  and  $KKS$ —hence the molecular formula is not less than  $H_2S$ . But compounds of selenion and tellurium with hydrogen, analogous in general properties to sulphuretted hydrogen, are known; from the marked similarity between these two elements and sulphur it is very probable that the molecular formulæ of the two compounds in question are  $H_2Se$  and  $H_2Te$  respectively: as these formulæ satisfy the analytical numbers, they may be adopted. But if similar reasoning is applied to the cases of aluminum and indium—metals which are closely related—it leads to a false conclusion: aluminum chloride is represented by the formula  $Al_2Cl_6$ , hence the minimum molecular formula of indium chloride is probably  $In_2Cl_6$ ; but this body has been recently gasified and shewn to have the molecular formula  $InCl_3$ .

The formula for water was once written  $HO$ . If potassium is thrown on to water, the solid product of the reaction is a white salt whose formula may be written  $HO.KO$  ( $O = 8$ ). But this substance is undecomposed by heat, and it exhibits none of the reactions which a compound of water with a metallic oxide might be expected to possess, nevertheless it contains hydrogen, oxygen and potassium; when it is fused with potassium, hydrogen is evolved and potassium oxide remains. The oxygen in this substance cannot be removed in parts. If the molecular formula of water is written  $H_2O$  ( $O = 16$ ) these facts are explained; the white solid then becomes  $KHO$ , and this formula—as the minimum molecular formula of the compound—is confirmed by the close analogies which exist between the properties of this body and those of alcohol, the molecular formula of which has been determined to be  $(C_2H_5)OH$ . If water is acted on by chlorine or bromine, the simplest formula for the compound produced is  $HCl$  (or  $HBr$ );

no compound is formed with evolution of oxygen and containing oxygen, hydrogen, and chlorine (or bromine); this formula— $\text{HCl}$ —is recognised on other grounds as the molecular formula of hydrochloric acid. Hence, it is argued, the hydrogen in the molecule of water is divisible in chemical changes into two parts, but the oxygen is not divisible, and hence, the simplest molecular formula for water is  $\text{H}_2\text{O}$ ; but if this is so, the atomic weight of oxygen cannot be less than 16.

Assuming the atomic weights of iron and oxygen to be (in round numbers) 56 and 16 respectively, the formula  $\text{Fe}_2\text{O}_3$  is deduced, from analyses, for ferric oxide as representing the smallest quantity of this compound which neutralises acids, forms double salts, can be acted on by chlorine to form  $\text{Fe}_2\text{Cl}_6$  &c.; hence this formula represents the minimum molecular weight of ferric oxide. But similar reasoning leads to  $\text{As}_2\text{O}_3$  as the minimum molecular formula of arsenious oxide; now we know that the gaseous oxide has a molecular weight expressed by the formula  $\text{As}_4\text{O}_6$ . Hence the method of analogies does not always lead to the adoption of the true molecular weight of a compound.

Sometimes the method of analogies becomes very indirect. Thus, the molecular formula of ferric chloride is  $\text{Fe}_2\text{Cl}_6$ , that of ferrous chloride is either  $\text{FeCl}_2$  or  $\text{Fe}_2\text{Cl}_4$ . Ferric chloride is produced by the action of chlorine on ferrous chloride; now the general action of chlorine is either to add itself on to other molecules, or to decompose molecules and then substitute itself for some one or more of the atoms formerly constituting these molecules. If ferrous chloride is  $\text{FeCl}_2$ , the action of chlorine on this molecule is represented by the equation  $2\text{FeCl}_2 + \text{Cl}_2 = \text{Fe}_2\text{Cl}_4$ , but this reaction is abnormal. If ferrous chloride is  $\text{Fe}_2\text{Cl}_4$ , the action of chlorine is represented by the equation  $\text{Fe}_2\text{Cl}_4 + \text{Cl}_2 = \text{Fe}_2\text{Cl}_6$ , and this reaction is analogous to other actions of this element; hence the molecular formula of ferrous chloride is probably not smaller than  $\text{Fe}_2\text{Cl}_4$ <sup>1</sup>.

<sup>1</sup> V. Meyer has recently obtained results regarding the vapour density of ferrous chloride which seem to him to point to the conclusion that, like stannous chloride,

The chemical method of determining minimum molecular weights, as applied to acids and bases, generally resolves itself into determining the basicity of the acid, or the acidity of the base. Thus, the results of analyses of sulphuric acid are satisfied by the formula  $H_{2x}S_xO_{4x}$ ; the fact that this acid is dibasic leads with a fair degree of certainty to the conclusion that  $x=1$ , and that the molecular formula of the compound is therefore  $H_2SO_4$ . The simplest formula which can be given to citric acid consistently with analytical results, and with the atomic weights  $C=12$ ,  $O=16$ ,  $H=1$ , is  $C_6H_8O_7$ ; that the molecular formula is probably not greater than this is shewn by the tribasic character of the acid. Reasons have been already given for adopting  $NH_3$  as the molecular formula of ammonia: analysis shews that the alkaloid quinine cannot have a smaller molecular weight than that represented by the formula  $C_{10}H_{11}NO$  ( $C=12$ ,  $H=1$ ,  $N=14$ ,  $O=16$ ), but the quantity of this alkaloid which neutralises that amount of hydrochloric acid which is neutralised by  $NH_3$ , is  $2C_{10}H_{11}NO$ , therefore the molecular formula of quinine is probably not less than  $C_{20}H_{22}N_2O_2$ .

This method may be also applied to determine the formulæ of salts. Thus if sulphuric acid has the molecular formula  $H_2SO_4$ , the molecule of sodium sulphate is probably represented by the formula  $Na_2SO_4$ , because the atom of sodium being very probably monovalent<sup>1</sup>, the amount of sodium 'equivalent' to  $H_2$  is represented by  $Na_2$ . So, although boric acid is non-volatile, its ethyl salt has been vaporised and found to have the formula  $(C_2H_5)_3BO_3$ , hence, knowing that boric acid is tribasic, we deduce for it the probable molecular formula  $H_3BO_3$ .

The so-called 'law of even numbers' enunciated by Gerhardt led to the revision of many molecular formulæ: Gerhardt stated that the sum of certain elementary atoms (hydrogen, chlorine and its analogues, nitrogen and its ana-

this compound possesses two molecular weights expressed respectively by the formulæ  $FeCl_2$  and  $Fe_2Cl_4$ ; *Ber.* 14. 1455.

<sup>1</sup> That is, capable of combining directly with not more than one atom of hydrogen, chlorine, bromine, iodine, or fluorine to form a compound molecule. See chap. II., pars. 56, 57.

logues) contained in any molecule is always an even number<sup>1</sup>. Thus analysis leads to the formula  $C_4H_6O_6$  for tartaric acid, and as the acid is dibasic this formula is apparently molecular; but the hydrogen atoms must be expressed by an even number according to Gerhardt's law, therefore the formula was doubled. Similar reasoning applied to the formulæ of nitric oxide and indium chloride would require that these should be written  $N_2O_2$  and  $In_2Cl_2$  respectively, but we know that the molecular formulæ of these compounds are NO and  $InCl_2$ , hence Gerhardt's 'law' must be applied with care<sup>2</sup>.

37. The chemical methods for determining molecular and atomic weights differ in two main particulars from the physical methods which have been already discussed.

The chemical methods as a class do not attempt to distinguish between solids, liquids and gases—so far as the application of these methods is concerned the molecular weight of a solid, liquid or gaseous substance is the smallest quantity which takes part in a chemical reaction—the physical method for finding molecular weights is only applicable in any strictness to gases.

The chemical methods also generally begin by determining, if possible, the atomic weights of the elements composing a given compound, and then argue as to the molecular weight of the compound; the physical method, on the other hand, begins by defining molecule, and then, applying this definition to chemical reactions, arrives at a definition of atom, both definitions being so stated as to indicate the data which are required before the relative weights of either atoms or molecules can be determined.

38. In the following table I have sought to summarise a considerable amount of facts concerning the atomic weights of the elements: it is well that the student should have placed before him a synopsis of the evidence on which these all-important numbers are based.

<sup>1</sup> See Laurent, *Chemical Method*, p. 46 *et seq.*


<sup>2</sup> For further examples of the application of chemical methods to determinations of molecular and atomic weights see Watts's *Dict.* vol. 1. pp. 457—8 and 460—1; also Williamson 'On the Atomic Theory,' *C. S. Journal*, 22. 328.



*Atomic Weights of the Elements.*

I	II	III	IV
<i>Element</i>	<i>Principal compounds, vapour densities of which have been determined</i>	<i>Specific heat: how determined</i>	<i>Isomorphism: compounds compared</i>
			[See note A, p. 84.]
HYDROGEN	HF, HCl, HBr, HI, H <sub>2</sub> S, H <sub>2</sub> Se, H <sub>2</sub> Te, H <sub>2</sub> N, H <sub>2</sub> P, H <sub>2</sub> C, &c.	indirectly [from sp. heat of H <sub>2</sub> O, NH <sub>4</sub> Cl, NH <sub>4</sub> NO <sub>3</sub> ] [atomic heat abnormal?]	—
LITHIUM	none	directly	Li compounds with analogous compounds of alkali metals
BERYLLIUM	none	directly: not finally settled	a few Be compounds with analogous compounds of Cd and Zn
BORON	BF <sub>3</sub> , BCl <sub>3</sub> , BBr <sub>3</sub> , B(CH <sub>3</sub> ) <sub>3</sub>	directly: sp. heat varies much with temperature	—
CARBON	CH <sub>4</sub> , CH <sub>2</sub> F <sub>2</sub> , CH <sub>2</sub> Cl <sub>2</sub> , CH <sub>2</sub> Br, CH <sub>2</sub> I, CHCl <sub>3</sub> , CO, CO <sub>2</sub> , COCl <sub>2</sub> , COS, CS <sub>2</sub> , CHN, C <sub>2</sub> H <sub>2</sub> O, C <sub>2</sub> H <sub>4</sub> O, &c.	directly: sp. heat varies much with temperature	CN compounds with those of F, Cl, Br and I
NITROGEN	NH <sub>3</sub> , NO, NO <sub>2</sub> , NOCl, N <sub>2</sub> O, N <sub>2</sub> O <sub>4</sub> , &c.	indirectly: very undecided [from sp. ht. of various compounds]	NH <sub>4</sub> compounds with those of alkali metals
OXYGEN	OH <sub>2</sub> , ON <sub>2</sub> , OC, OCl <sub>2</sub> P, O <sub>3</sub> C, O <sub>3</sub> S, O <sub>3</sub> Se, O <sub>3</sub> As, &c.	indirectly: very undecided [from sp. ht. of various compounds]	—
FLUORINE	FH, F(CH <sub>3</sub> ) <sub>2</sub> , F <sub>2</sub> B, F <sub>2</sub> Si, F <sub>2</sub> P, &c.	indirectly: very undecided [from sp. ht. of CaF <sub>2</sub> , &c.]	metallic fluorides with analogous compounds of Cl, Br and I
SODIUM	none	directly	Na compounds with those of other alkali metals
MAGNESIUM	none	directly	Mg compounds generally with those of Zn, Mn, and Fe (in ferrous salts)
ALUMINIUM	Al <sub>2</sub> Cl <sub>3</sub> , Al <sub>2</sub> Br <sub>3</sub> , Al <sub>2</sub> I <sub>3</sub>	directly	with Cr, Mn and Fe in R <sub>2</sub> O <sub>3</sub> and derivatives
SILICON	SiF <sub>4</sub> , SiCl <sub>4</sub> , SiH <sub>4</sub> , Si(CH <sub>3</sub> ) <sub>4</sub> , SiH <sub>2</sub> Cl <sub>2</sub> , Si <sub>2</sub> OCl <sub>2</sub> , Si <sub>2</sub> O(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	directly: sp. ht. varies much with temperature	with C, Zr, Sn and Ti in compounds of type RO <sub>2</sub>
PHOSPHORUS	PH <sub>3</sub> , PCl <sub>3</sub> , PI <sub>3</sub> , PF <sub>3</sub> , POCl <sub>3</sub> , PSCl <sub>3</sub> , P <sub>2</sub> I <sub>4</sub> , P <sub>2</sub> H <sub>4</sub> , P <sub>2</sub> N <sub>2</sub> Cl <sub>4</sub> , &c.	directly	phosphates with vanadates and arsenates, organic compounds of P with those of N, As and Sb
SULPHUR	SH <sub>2</sub> , SO <sub>2</sub> , SO <sub>3</sub> , SOCl <sub>2</sub> , S <sub>2</sub> C, S <sub>2</sub> Cl <sub>2</sub> , &c.	directly	with Se compounds, with Te compounds of type R <sup>+</sup> Te. Salts of H <sub>2</sub> SO <sub>4</sub> with those of H <sub>2</sub> SeO <sub>4</sub> and H <sub>2</sub> TeO <sub>4</sub>
CHLORINE	ClH, Cl(CH <sub>3</sub> ) <sub>3</sub> , ClTi, Cl <sub>2</sub> Zn, Cl <sub>2</sub> Hg, Cl <sub>2</sub> Hc, Cl <sub>2</sub> Bi, Cl <sub>2</sub> Sb, Cl <sub>2</sub> C, Cl <sub>2</sub> Si, Cl <sub>2</sub> Ti, Cl <sub>2</sub> Ta, Cl <sub>2</sub> Mo, Cl <sub>2</sub> W, &c.	indirectly: doubtful [from comparison of specific heats of various haloid compounds]	Chlorides, with analogous compounds of Br and I
POTASSIUM	none	directly	K compounds with those of other alkali metals
CALCIUM	none	directly	Ca compounds with those of Sr, Ba, and in some cases Pb
SCANDIUM	none	sp. heats of some compounds determined	[? Sc compounds with those of other earth metals]
TITANIUM	TiCl <sub>4</sub>	sp. heats of a few compounds determined	TiO <sub>2</sub> , and some derivatives with analogous compounds of C, Si, Zr, Sn and Th
VANADIUM	VCl <sub>3</sub> , VOCl <sub>3</sub>	sp. heats of one or two compounds determined	Vanadates with phosphates and arsenates

*Atomic Weights of the Elements.*

V Atomic weight		VI	VII	VIII
(1) by vapour density method	(2) by sp. heat method	Compounds analysed, &c. in order to find combining weight of the element	Combining weight	Remarks
[For more details concern- ing these numbers see Tables, pp. 37-40 and pp. 42-49.]		[See note B, p. 84.]		[See note C, p. 84.]
I				
—	7'01	1 Lithium chloride	7'01	
—	9'08	2 Beryllium sulphate	4'54	
10'95	10'95	3 Borax, boron chloride	3'65	
11'97	11'97	4 Diamond burnt to CO <sub>2</sub>	2'99	
14'01	—	5 Ammonium chloride, silver nitrate	4'67	
15'96	—	6 Synthesis of water	7'98	
19'1	—	7 Sodium fluoride, potassium fluoride, calcium fluoride	19'1	
—	23	8 Sodium chloride	23	
—	24	9 Magnesium sulphate, do. chloride, synthesis of mag- nesium sulphate	12	
27'02 [see p. 56]	27'02	10 Ammonia alum, aluminium bromide, solution of alumin- ium in soda	9'007	
28	28	11 Silicon chloride	7	
30'96	30'96	12 Phosphorus chloride, synthesis of phosphorus pentoxide	10'32	
31'93	31'98	13 Synthesis of silver sulphide, reduction of silver sulphate by hydrogen	10'66	
35'37	—	14 Potassium chlorate, synthesis of silver chloride	35'37	
—	39'04	15 Potassium chloride, do. bro- mide	39'04	
—	39'9	16 Calcium chloride, calcium car- bonate	19'95	
—	—	17 Synthesis of scandium sul- phate	14'68	<p>Sc. The atomic weight of this metal is most probably <math>14'68 \times 3 = 44'04</math>: If this is so, the oxide is written Sc<sub>2</sub>O<sub>3</sub> and is thus shewn to be analogous with the oxides of the earth metals.</p>
48	—	18 Titanium chloride, bromide and oxide	12	
51'2	—	19 Vanadium pentoxide, do. oxy- chloride	12'8	

*Atomic Weights of the Elements.*

I  <i>Element</i>	II  <i>Principal compounds, vapour densities of which have been determined</i>	III  <i>Specific heat : how determined</i>	IV  <i>Isomorphism : compounds compared</i>  [See note A, p. 84.]
CHROMIUM	$\text{CrO}_2\text{Cl}_2$	directly [? too low]	Salts of $\text{H}_2\text{CrO}_4$ with those of $\text{H}_2\text{MnO}_4$ and $\text{H}_2\text{TeO}_4$ , $\text{Cr}_2\text{O}_3$ with $\text{Al}_2\text{O}_3$ , $\text{Mn}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ , $\text{Mn}_2\text{O}_3$ with $\text{Al}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ , $\text{R}_2\text{MnO}_4$ with $\text{R}_2\text{CrO}_4$ and $\text{R}_2\text{TeO}_4$ , $\text{RMnO}_4$ with $\text{KClO}_4$ , $\text{Fe}_2\text{O}_3$ and derivatives with $\text{Al}_2\text{O}_3$ , $\text{Cr}_2\text{O}_3$ , $\text{Mn}_2\text{O}_3$ and derivatives, some Fe salts with those of Ni, Co, and Cu
MANGANESE	none	directly [? too high]	
IRON	$\text{Fe}_2\text{Cl}_6$	directly	
NICKEL	none	directly	
COBALT	none	directly	Ni with Co compounds, some Ni compounds with those of Fe (ferrous salts) Co with Ni compounds, some Co compounds with those of Fe (ferrous salts)  most Cu compounds with those of Ni and Co, some with Fe (ferrous) compounds, Cu with Ag compounds of type $\text{R}_2\text{O}$ Zn compounds with those of Mg and Mn Ga alum with other alums
COPPER	$\text{Cu}_2\text{Cl}_2$	directly	
ZINC	$\text{ZnCl}_2$ , $\text{Zn}(\text{CH}_3)_2$ , $\text{Zn}(\text{C}_2\text{H}_5)_2$	directly	
GALLIUM	$\text{Ga}_2\text{Cl}_4$	directly [? too low]	
ARSENIC	$\text{AsH}_3$ , $\text{AsCl}_3$ , $\text{AsI}_3$ , $\text{As}(\text{CH}_3)_2\text{Cl}$ , $\text{As}_4\text{O}_6$ , &c.	directly	As compounds with those of Sb and Bi, organic compounds of As with those of N, P, and Sb, arsenates with phosphates and vanadates Se with S compounds  Bromides with analogous compounds of Cl and I Rb compounds with those of other alkali metals
SELENION	$\text{SeH}_2$ , $\text{SeO}_2$	directly	
BROMINE	$\text{BrH}$ , $\text{Br}(\text{CH}_3)$ , $\text{Br}_2\text{Cd}$ , $\text{Br}_2\text{B}$ , $\text{Br}_2\text{Sn}$ , $\text{Br}_2\text{U}$ , &c.	directly	
RUBIDIUM	none	indirectly : doubtful [from comparison of specific heats of some compounds with those of other alkali metals]	
STRONTIUM	none	indirectly : doubtful [comparison of specific heats of compounds of Sr, Ca, and Ba]	Sr compounds with those of Ca and Ba, and with some Pb salts  Yt compounds with those of other earth metals  $\text{ZrO}_2$ with $\text{TiO}_2$ , $\text{ThO}_2$ , $\text{SnO}_2$ and $\text{SiO}_2$ Nb with Ta compounds, Nb fluorides and oxyfluorides with Mo do. do. Mo with W compounds, some salts of $\text{H}_2\text{MoO}_4$ with those of $\text{H}_2\text{CrO}_4$ , Mo with Nb fluorides and oxyfluorides
YTTRIUM	none	sp. heats of a few compounds determined	
ZIRCONIUM	$\text{ZrCl}_4$	directly [? too low]	
NIوبيUM	$\text{NbCl}_5$ , $\text{NbOCl}_3$	—	
MOLYBDENUM	$\text{MoCl}_5$	directly [? too high]	

*Atomic Weights of the Elements.*

V <i>Atomic weight</i>		VI <i>Compounds analysed, &amp;c. in order to find combining weight of the element</i>	VII <i>Combining weight</i>	VIII <i>Remarks</i>
(1) <i>by vapour density method</i>	(2) <i>by sp. heat method</i>			
[for more details concerning these numbers see Tables, pp. 37-40 and pp. 48-49.]		[See note B, p. 84.]		[See note C, p. 84.]
52.4	52.4	<sup>20</sup> Chromium chloride, silver chromate, potassium dichromate	26.2	
—	55	<sup>21</sup> Manganese chloride, manganous-manganic oxide, manganous oxalate, silver permanganate, &c.	27.5	
55.9 [see p. 56]	55.9	<sup>22</sup> Synthesis of ferric oxide, reduction of ferric oxide, analysis of ferrous and ferric chlorides	27.95	
—	58.6	<sup>23</sup> Nickel chloride, nickelous oxide, strychnine-nickel cyanide, brucine-nickel cyanide, &c.	29.3	
—	59	<sup>24</sup> Ammonium-cobalt cyanide, phenyl-ammonium cobalt cyanide, strychnine and brucine-cobalt cyanides	29.5	
63.4 [see p. 56]	63.4	<sup>25</sup> Reduction of copper oxide, electrolysis of copper sulphate, &c.	31.7	
64.9	64.9	<sup>26</sup> Synthesis of zinc oxide, analysis of potassium-zinc chloride	32.3	
69 [see p. 56]	69	<sup>27</sup> Oxidation of the metal, analysis of gallium-ammonia alum	23	
74.9	74.9	<sup>28</sup> Arsenic bromide, do. chloride, do. oxide	24.97	
78.8	78.8	<sup>29</sup> Reduction of selenion dioxide, reduction of silver selenite	39.4	
79.75	79.75	<sup>30</sup> Synthesis of silver bromide, analysis of potassium bromide	79.75	
—	—	<sup>31</sup> Rubidium chloride	85.2	<i>Rb.</i> From analogies between Rb (and its salts) and the metals of the alkalis, the formulæ RbCl, Rb <sub>2</sub> O, &c. are most probably correct: if so, the atomic weight of Rb is to be taken as equal to its combining weight.
—	—	<sup>32</sup> Strontium chloride	43.65	<i>Sr.</i> The atomic weight of strontium must be taken as $43.65 \times 2 = 87.3$ if the formulæ of its salts are to become analogous to those of the Ba and Ca salts.
—	—	<sup>33</sup> Synthesis of yttrium sulphate	29.87	<i>Yt.</i> Atomic weight probably = $29.87 \times 3 = 89.6$ because of analogy of Yt salts with those of earth metals.
90	90	<sup>34</sup> Zirconium chloride, potassium-zirconium fluoride	45	
94	—	<sup>35</sup> Niobium chloride, potassium-niobium oxyfluoride	31.32	
95.8	95.8	<sup>36</sup> Molybdenum dichloride, tetrachloride and pentachloride	19.16	

*Atomic Weights of the Elements.*

I	II	III	IV
<i>Element</i>	<i>Principal compounds, vapour densities of which have been determined</i>	<i>Specific heat : how determined</i>	<i>Isomorphism : compounds compared</i>
			[See note A, p. 84.]
RHODIUM	none	directly	most Rh compounds with those of Ru, Pd, Ir, Pt and Os
RUTHENIUM	none	directly	most Ru compounds with those of Rh, Pd, Ir, Pt and Os
PALLADIUM	none	directly	most Pd compounds with those of Ru, Rh, Ir, Pt and Os
SILVER	none	directly	some Ag compounds with those of Na and other alkali metals, Ag <sub>2</sub> with Cu compounds of type R <sub>2</sub> O, a few Ag and Au compounds
CADMIUM	CdBr <sub>2</sub>	directly	some Cd compounds with those of Be and Zn
INDIUM	InCl <sub>3</sub>	directly	some In compounds with those of Cd and Be
TIN	SnCl <sub>2</sub> , SnCl <sub>4</sub> , Sn <sub>2</sub> Cl <sub>4</sub>	directly	SnO <sub>2</sub> with TiO <sub>2</sub> , ZrO <sub>2</sub> and ThO <sub>2</sub>
ANTIMONY	SbH <sub>3</sub> , SbCl <sub>3</sub> , SbF <sub>3</sub> , Sb(CH <sub>3</sub> ) <sub>3</sub>	directly	Sb compounds with those of As and Bi
IODINE	IH, ICl, I(CH <sub>3</sub> ) <sub>2</sub> , I <sub>2</sub> P <sub>4</sub> , I <sub>2</sub> Hg, I <sub>2</sub> P, I <sub>2</sub> As, I <sub>2</sub> Si, I <sub>2</sub> Al, &c.	directly	Iodides with analogous compounds of Cl and Br
TELLURIUM	Tell <sub>2</sub>	directly	most Te compounds with those of S and Se
CÆSIUM	none	indirectly: doubtful [comparison of specific heats of compounds with those of other alkali metals]	Cs compounds with those of other metals of alkalis
BARIUM	none	indirectly: doubtful [comparison of specific heats of compounds of Ca, Sr, and Ba]	Ba compounds with those of Ca and Sr
LANTHANUM	none	directly	most La compounds with those of Ce, Di, Er and Yt, some compounds of these metals with Cr compounds
CERIUM	none	directly	
DIDYMIUM	none	directly	
ERBIUM	none	sp. heats of a few compounds determined	
YTTERBIUM	none	sp. heats of a few compounds determined	[? a few Yb compounds with those of other earth metals]
TANTALUM	TaCl <sub>5</sub>	—	Ta with Nb compounds
TUNGSTEN	WOCl <sub>6</sub> , WCl <sub>6</sub> , WCl <sub>4</sub>	directly	W with Mo compounds, some salts of H <sub>2</sub> WO <sub>4</sub> with those of H <sub>2</sub> CrO <sub>4</sub> and H <sub>2</sub> TcO <sub>4</sub>
IRIDIUM	none	directly	Os, Ir and Pt compounds with those of Ru, Rh and Pd
OSMIUM	OsO <sub>4</sub>	directly	
PLATINUM	none	directly	

*Atomic Weights of the Elements.*

V Atomic weight		VI	VII	VIII
(1) by vapour density method	(2) by sp. heat method	Compounds analysed, &c. in order to find combining weight of the element	Combining weight	Remarks
[for more details concern- ing these numbers see Tables, pp. 37-40 and pp. 48-49.]		[See note B, p. 84.]		[See note C, p. 84.]
—	104	<sup>37</sup> Potassium-rhodium chloride	26	
—	(103)	<sup>37a</sup> Purpureo-rhodium chloro- and bromo-compounds)	(25.75)	
—	104.5	<sup>38</sup> Potassium-ruthenium chloride	26.1	
—	106.2	<sup>39</sup> Palladium chloride	26.55	
—	107.66	<sup>40</sup> Silver chlorate, bromate, iodate, synthesis of silver bromide and iodide	107.66	
112	112	<sup>41</sup> Cadmium bromide	56	
113.4	113.4	<sup>42</sup> Synthesis of indium oxide	37.8	
117.8	117.8	<sup>43</sup> Synthesis of stannic oxide	58.9	
120	120	<sup>44</sup> Antimony bromide, reduction of antimony oxide, also analy- sis of antimony sulphide	40	
126.53	126.53	<sup>45</sup> Silver iodate, silver iodide, synthesis of do.	126.53	
(?) 127.5	(?) 127.5	<sup>46</sup> Oxidation of tellurium, analy- sis of potassium - tellurium bromide	63.75	<i>Te.</i> Very possibly the atomic weight of Te is less than that of iodine. [See note on p. 87.]
—	—	<sup>47</sup> Cæsium chloride	132.7	<i>Cs.</i> This metal certainly belongs to the alkali metals—hence the chloride is CsCl, and, if so, the atomic wt. = 132.7.
—	—	<sup>48</sup> Barium chloride	68.43	<i>Ba.</i> Atomic weight probably 68.43 × 2 = 136.86 because of analogies be- tween salts of Ba, Sr and Ca.
—	138.5	<sup>49</sup> Lanthanum sulphate, do. ox- ide, do. oxalate	46.17	
—	141	<sup>50</sup> Cerium oxalate	47	
—	144	<sup>51</sup> Didymium oxide and sulphate	48	
—	(142)	<sup>51a</sup> " " "	47.6	
—	—	<sup>52</sup> Erbium sulphate	55.33	<i>Er.</i> This metal belongs to the earth group, hence the atomic weight is taken as 55.33 × 3 = 166.
—	—	<sup>53</sup> Ytterbium sulphate	57.69	<i>Yb.</i> For similar reasons to those which apply in cases of Sc, Yt and Er, the atomic weight of Ytterbium is supposed to be 3 times its combin- ing weight (= 173).
182	—	<sup>54</sup> Potassium-tantalum fluoride, ammonium-tantalum fluoride	60.67	
183.6	183.6	<sup>55</sup> Reduction of tungstic oxide, analysis of tungsten hexchlor- ide	30.6	
—	192.5	<sup>56</sup> Potassium-iridium chloride	48.13	
193	193	<sup>57</sup> Osmium tetroxide	48.25	<i>Os.</i> The number given is calculated from 2 determinations of vapour density of OsO <sub>4</sub> by Deville and Debray, other experimenters have found numbers for atomic weight of this metal varying from 195 to 199.
—	194.3	<sup>58</sup> Potassium-platinum chloride	48.575	

*Atomic Weights of the Elements.*

I	II	III	IV
<i>Element</i>	<i>Principal compounds, vapour densities of which have been determined</i>	<i>Specific heat; how determined</i>	<i>Isomorphism: compounds compared</i>  [See note A, p. 84.]
GOLD	none	directly	some Au compounds with those of Ag, a few Au compounds with those of Ni and Fe
MERCURY	[HgCl] <sub>2</sub> HgCl <sub>2</sub> HgI <sub>2</sub> , Hg(CH <sub>3</sub> ) <sub>2</sub> , &c.	directly	Hg and Cu compounds of type RO
THALLIUM	TlCl	directly	Tl compounds with those of Pb of type RCl <sub>2</sub> , Tl compounds of type TlCl with those of alkali metals
LEAD	PbCl <sub>2</sub> , Pb(CH <sub>3</sub> ) <sub>4</sub>	directly	some Pb with Tl compounds, many Pb with Cu and Hg compounds
BISMUTH	BiCl <sub>3</sub> , BiF <sub>3</sub> , Bi(CH <sub>3</sub> ) <sub>3</sub> , &c.	directly	Bi compounds with those of As and Sb
THORIUM	none	directly	ThO <sub>3</sub> with SiO <sub>2</sub> , TiO <sub>2</sub> , SnO <sub>2</sub> and ZrO <sub>2</sub>
URANIUM	UCl <sub>4</sub> , UBr <sub>4</sub>	directly	some compounds of type UO <sub>3</sub> , with those of Al, Cr, Mn and Fe

*Notes to Table of Atomic Weights.*

A. As the method based on isomorphism of compounds is chiefly used as a means of verifying values assigned to atomic weights by other methods, no numbers are given in column IV., but merely an indication of the various compounds which have been compared crystallographically, and on which, arguments for or against a given value for the atomic weights in column V. have been, or may be, based.

B. This column (VI.) is not to be regarded as containing anything like a complete summary of the processes employed for determining the combining numbers of the elements; only the more important processes are indicated;—references are given to the original papers.

A complete account of all researches on this subject will be found in *A Recalculation of the Atomic Weights*, by F. W. Clarke [Part V. of the *Constants of Nature* published by the Smithsonian Institution], and also in *Die Atomgewichte der Elemente*, by L. Meyer and K. Seubert [Leipzig, 1883].

C. When the atomic weight given in column V. section (2) is a multiple of the combining number in column VII., no number being given in section (1) of column V., it is to be inferred that, besides the argument drawn from the value of the specific heat of the element in question, there are other chemical reasons for adopting the special multiple which appears in V. (2): these reasons may be broadly described as based on analogies between salts of the given element and salts of other elements, the atomic weights of which have been established by the two leading physical methods.

*Atomic Weights of the Elements.*

V Atomic weight		VI	VII	VIII
(1) by vapour density method	(2) by sp. heat method	Compounds analysed, &c. in order to find combining weight of the element	Combining weight	Remarks
[For more details concerning these numbers see Tables, pp. 37-40 and pp. 48-49.]		[See note B, p. 84.]		[See note C, p. 84.]
—	196	<sup>20</sup> Gold chloride, potassium-gold chloride	65.33	
199.8	199.8	<sup>21</sup> Mercuric chloride, do. oxide	99.9	
203.64	203.64	<sup>61</sup> Synthesis of thallium nitrate	203.64	
206.4	206.4	<sup>62</sup> Synthesis of lead nitrate, do. do. sulphate	103.2	
208	208	<sup>63</sup> Synthesis of bismuthous oxide, &c., analysis of bismuthous chloride	69.33	
—	232.4	<sup>64</sup> Thorium sulphate	58.1	
240	240	<sup>65</sup> Uranium acetate, do. oxalate	60	

*References to Table of Atomic Weights.*

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<sup>2</sup> Be. NILSON and PETTERSSON, *Ber.* **13**. 1451.

<sup>3</sup> B. BERZELIUS, *Pogg. Ann.* **2**. 129. DEVILLE, *Ann. Chim. Phys.* (3) **55**. 180.

<sup>4</sup> C. DUMAS and STAS, *Ann. Chim. Phys.* (3) **1**. 5. ERDMANN and MARCHAND, *J. für pract. Chemie*, **23**. 159. ROSCOE, *Compt. rend.* **94**. 1180.

<sup>5</sup> N. STAS, *Rapports*, pp. 50, 87, 92; and *Nouvelles Recherches*, pp. 57, 281.

<sup>6</sup> O. ERDMANN and MARCHAND, *J. für pract. Chemie*, **26**. 468. DUMAS, *Ann. Chim. Phys.* (3) **8**. 189.

<sup>7</sup> F. LOUYET, *Ann. Chim. Phys.* (3) **25**. 291. DUMAS, do. (3) **55**. 170. DE LUCA, *Compt. rend.* **51**. 299.

<sup>8</sup> Na. PELOUZE, *Compt. rend.* **20**. 1050. DUMAS, *Ann. Chim. Phys.* (3) **55**. 182. STAS, *Rapports*, p. 78; and *Nouvelles Recherches*, p. 248.

<sup>9</sup> Mg. JACQUELAIN, *Ann. Chim. Phys.* (3) **32**. 202. BAHR, *J. für pract. Chemie*, **56**. 310. DUMAS, *Ann. Chim. Phys.* (3) **55**. 187. MARIGNAC, *Archiv. Scien. Phys. nat.* (3) **10**. 5, 193.

<sup>10</sup> Al. J. W. MALLET, *Phil. Trans. for 1880*. 1003 et seq.

<sup>11</sup> Si. PELOUZE, *Compt. rend.* **20**. 1052. DUMAS, *Ann. Chim. Phys.* (3) **55**. 183. J. SCHIEL, *Annalen*, **120**. 94.

<sup>12</sup> P. PELOUZE, *Compt. rend.* **20**. 1053. SCHRÖTTER, *Ann. Chim. Phys.* (3) **55**. 131. DUMAS, *Ann. Chim. Phys.* (3) **55**. 172.

<sup>13</sup> S. STAS, *Rapports*, p. 53.



- <sup>14</sup> Cl. STAS, *Rapports*, pp. 38, 42, 44, 118; and *Nouvelles Recherches*, p. 208.
- <sup>15</sup> K. STAS, *Rapports*, pp. 69, 91, 118; and *Nouvelles Recherches*, p. 244.
- <sup>16</sup> Ca. BERZELIUS, *Pogg. Ann.* 8. 189. DUMAS, *Ann. Chim. Phys.* (3) 55.
190. ERDMANN and MARCHAND, *Annalen*, 44. 216: 52. 210: 76. 219. SALVÉTEL, *Compt. rend.* 17. 318.
- <sup>17</sup> Sc. NILSON, *Ber.* 13. 1439.
- <sup>18</sup> Ti. H. ROSE, *Pogg. Ann.* 15. 145. J. PIERRE, *Ann. Chim. Phys.* (3) 20.
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- <sup>24</sup> Co. WESELSKY, *Ber.* 2. 592. R. H. LEE, *Ber.* 4. 789. RUSSELL, *loc. cit.*
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- <sup>29</sup> Se. PETTERSSON and EKMAN, *Ber.* 9. 1210.
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- <sup>32</sup> Sr. MARIGNAC, *Annalen*, 106. 168. DUMAS, *Ann. Chim. Phys.* (3) 55. 191.
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- <sup>40</sup> Ag. STAS, *Rapports*, pp. 38, 42, 44; and *Nouvelles Recherches*, pp. 109, 158, 171, 189, 193, 208.
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- <sup>53</sup> *Yb.* NILSON, *Ber.* **12**. 550 : **13**. 1430.
- <sup>54</sup> *Ta.* MARIGNAC, *Annalen*, *Supplbd.* **4**. 351.
- <sup>55</sup> *W.* ROSCOE, *Chem. News*, **25**. 61, 73.
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- <sup>57</sup> *Os.* DEVILLE and DEBRAY, *Ann. Chim. Phys.* (3) **56**. 403.
- <sup>58</sup> *Pt.* K. SEUBERT, *Ber.* **14**. 865. [*Annalen*, **207**. 29.]
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*Note.* The full titles of Stas's treatises which are referred to in this table are: (1) *Recherches sur les rapports reciproques des poids atomiques*, par J. S. Stas, Bruxelles, 1860. (2) *Nouvelles recherches sur les lois des proportions chimiques, sur les poids atomiques et leur rapports mutuels*, par J. S. Stas, Bruxelles, 1865. A translation into German of both treatises was published in 1867 under the title *Untersuchungen über die Gesetze der Chemischen Proportionen, über die Atomgewichte und ihre gegenseitigen Verhältnisse*.

<sup>1</sup> BRAUNER (see abstract in *Ber.* **18**. 3053) has recently obtained values for the atomic weight of Tellurium varying from 124.94 to 125.4 (mean = 125); he has shewn that the process employed by Wills gives values which are too high, unless great precautions are taken.

## CHAPTER II.

### ATOMIC AND MOLECULAR SYSTEMS.

#### SECTION I. *Nascent Actions.*

39. BRODIE applied his hypothesis regarding the structure of elementary molecules (see *ante*, p. 71, par. 36) to explain a number of phenomena generally grouped together under the name *nascent actions*. That explanation, somewhat simplified and also developed by subsequent research, is usually regarded as the most satisfactory that can be given in the present state of knowledge.

When hydrogen is passed into water containing silver chloride in suspension no chemical change occurs; when hydrogen is generated in the vessel which contains the silver chloride decomposition of this salt proceeds rapidly with production of silver and hydrochloric acid. Nitrobenzene is converted into aniline by the action of hydrogen produced in contact with it, but not by hydrogen produced in another vessel and conducted into that containing the nitrobenzene. Carbon, hydrogen, and nitrogen do not combine directly; but if electric sparks are passed through a mixture of benzene vapour and nitrogen, hydrocyanic acid is produced. Sulphur dioxide and water when heated with oxygen are only very partially changed into sulphuric acid; but if the oxygen is produced in contact with the moist dioxide (e.g. by decomposition of nitrogen trioxide) the change into sulphuric acid is

rapidly completed. Sulphur is not oxidised to sulphuric acid by bromine in presence of water; but if the sulphur is produced from a compound in presence of bromine water, it is then oxidised (e.g. sulphuretted hydrogen passed into bromine water gives hydrobromic acid and sulphur, and also sulphuric acid). Metallic chlorides (e.g. aluminium chloride) produced by the action of metal on chlorine only at very high temperatures, and in small quantities for a given time of action, are sometimes much more easily prepared by the action of chlorine on a mixture of the metallic oxide and carbon. The general action of metals on dilute cold sulphuric acid is to produce a sulphate and evolve hydrogen, but on nitric acid to produce a nitrate and evolve oxides of nitrogen, nitrogen and ammonia; many metals when heated with concentrated sulphuric acid evolve sulphur dioxide, either alone, or in some cases mixed with hydrogen and sulphuretted hydrogen.

40. These phenomena, and many others of the same class, find an explanation in terms of the molecular theory, that explanation being based on the distinction, already insisted on, between molecules and atoms. Any mass of a gaseous element under ordinary conditions is built up of molecules, but if we assume that when a compound molecule undergoes decomposition a short but appreciable time elapses before the greater number of the elementary atoms which composed it have rearranged themselves to form new molecules, we have the materials for a fairly satisfactory explanation of the phenomena of nascent action. This explanation does not necessitate, as some of its French opponents say it does, the assumption of strange and inexplicable properties as belonging to the elementary atoms. Indeed the existence of what is known as the 'nascent state' seems to follow as a necessary deduction from the molecular theory applied to chemical phenomena. When a chemical change occurs between two molecules, the first step in that change must in most cases consist in a breaking up of the molecular structures, and the second, in a rearrangement of the parts of the molecules, i.e. of the atoms, to form a configuration stable

under the conditions of the experiment : if, by the presentation of molecules of a third chemical substance, there is rendered possible the adoption by the various atoms of another configuration, more stable than that just supposed to be assumed, this, the most stable configuration, will be adopted. But if the earlier stable configuration has been assumed by the atoms, it does not follow that the introduction of the third class of molecules will *now* cause this configuration to become unstable<sup>1</sup>.

41. Following out this line of argument, it would appear probable that compounds should present phenomena somewhat analogous to those exhibited by elements when in the nascent, i.e. on the hypothesis now adopted, atomic state. Let it be supposed that no chemical change occurred when the compound molecules *a* and *b* were brought into contact, nevertheless if the atoms constituting these molecules were allowed to react a chemical change might occur. In a reaction wherein the given compound is produced there must be a moment of time when this compound can only be said to exist potentially, when the atoms which constitute its molecules have not settled down into stable configurations ; at this moment the compound may be said to exist in the nascent state. If the atomic vibrations and interactions are allowed to run what may be called their normal course, the compound molecules are certainly produced, but if these interactions are interfered with, a new set of molecules may be

<sup>1</sup> It may be urged that the energy (or part of the energy) which is used in decomposing the molecules of the reacting substances is gained by the atoms thence produced, and that the only difference between e.g. ordinary and 'nascent' hydrogen, is to be found in the greater chemical energy of the latter. The importance of this point of view is of course admitted by the upholders of the atomic explanation of nascent actions, but they would supplement this by the statement that the configuration with which the greater quantity of energy is associated is atomic, and they contrast this with a molecular and comparatively inactive configuration.

The experiments of Victor Meyer on iodine give direct evidence of the separation of elementary molecules into atoms by the addition of energy in the form of heat. (See *ante*, p. 31 par. 15.)

In book II. chapter II. will be found some facts regarding dissociation which bear on the subject of nascent actions.

formed, which molecules bear a more or less simple genetic relation to those produced in the normal process of chemical change<sup>1</sup>.

The following among other cases of chemical change find a partial explanation in terms of this hypothesis. Nitrous acid has no action on the primary mononitroparaffins ( $C_nH_{2n+1}.NO_2$ ), but these compounds are converted into nitrolic acids ( $C_nH_{2n}.N_2O_3$ ) by the action of potassium nitrite and sulphuric acid, i.e. by the action of potentially formed nitrous acid. Nitric acid does not act on naphthol to produce dinitronaphthol, but if naphthol be produced in contact with nitric acid—e.g. by boiling diazonaphthalene hydrochloride in presence of nitric acid—dinitronaphthol is formed. Carbon monoxide and ethylene do not react to form acrolein even under the influence of electric sparks, but if ethylene is exploded with a quantity of oxygen less than sufficient for complete oxidation, carbon monoxide is produced and simultaneously acrolein is formed, i.e. the chemical change proceeds partly in its normal way and at the same time the atoms of the 'nascent' carbon oxide react on the ethylene molecules with production of acrolein. When pariodophenol is fused with potash at  $163^\circ$  hydroquinone is produced, but at higher temperatures only resorcin is formed: now as fusing potash does not act on hydroquinone it seems necessary to conclude, that in the fusion of pariodophenol at high temperatures hydroquinone is produced, but is immediately changed into resorcin. Many olefines (e.g. amylene) are polymerised by the action of sulphuric acid: the most probable explanation of this action assumes that an unstable compound of olefine and sulphuric acid is produced and again decomposed, and that the molecules

<sup>1</sup> In all such considerations we can deal with molecular phenomena only by a statistical method, we can reason only as to the average condition of the mass of molecules constituting a substance at any moment of time.

It seems not improbable that there may sometimes be as great differences between the properties of a number of elementary atoms all of one kind and the elementary molecules which are produced by the union of these atoms, as between the properties of a number of atoms of different kinds and the compound molecules produced by the union of these atoms.

of olefine as they are set free from this compound coalesce to form polymeric molecules. By carrying the explanation a little further, and supposing that this coalescence of molecules is due to the interaction of the atoms, or possibly of groups of atoms, which under ordinary conditions would produce molecules of olefine, the phenomenon in question is brought under the general hypothesis of nascent state. I have myself shewn that bismuthic oxide ( $\text{Bi}_2\text{O}_3$ ) is reduced to bismuthous oxide ( $\text{Bi}_2\text{O}_3$ ) by heating in hydrogen at a temperature lower than that at which hypobismuthic oxide ( $\text{Bi}_2\text{O}_3$ ) is reduced to the same final state, and that hypobismuthic oxide is reduced to hypobismuthous oxide ( $\text{Bi}_2\text{O}_3$ ) at a temperature lower than that at which bismuthous oxide undergoes a similar change. I have also shewn that bismuthic oxide is more easily and completely deoxidised when heated in chlorine than bismuthous oxide. When the atoms composing bismuthic oxide molecules are shaken asunder, the action between these and hydrogen, or chlorine, proceeds until a stable configuration is reached; those points in the molecular series known as hypobismuthic and bismuthous oxide respectively, are passed through during the change, but the molecules of these compounds are only potentially, not actually formed: when however these molecules have been formed before chemical action begins, a higher temperature must be reached before the action actually occurs.

42. Whether or not a given phenomenon is to be explained by the particular application of the molecular theory now under consideration, must be decided by the nature of that phenomenon. Among phenomena which are usually but not invariably explained thus, those which occur in the decomposition of acids by metals are of great importance.

The products of the action of metals on sulphuric and nitric acid, respectively, have been already broadly stated. That no hydrogen is evolved in the case of nitric acid is generally sought to be explained by assuming that the hydrogen atoms are seized by the nitric acid and oxidised to water, with a corresponding reduction of the acid to oxides of nitrogen, nitrogen, and sometimes ammonia.

Direct proof in favour of this hypothesis has been given by Gladstone and Tribe<sup>1</sup>, who have shewn that when a small piece of magnesium is placed in a large excess of nitric acid (strengths 1 : 1 and 1 : 2—acid to water—were employed) the gas at first evolved consists of nearly pure hydrogen, but that oxides of nitrogen are very quickly produced. The same chemists<sup>2</sup> have established a close relation between the action on sulphuric and nitric acids of the hydrogen produced by electrolysis of these acids, and hydrogen occluded by platinum or palladium; they have also shewn that hydrogen evolved by the action of the copper zinc couple is very analogous in general reducing actions to hydrogen occluded by platinum or palladium.

When concentrated nitric acid is subjected to electrolysis no hydrogen is evolved, but the acid is reduced; when more dilute acid is used hydrogen is evolved, reduction of the acid also occurs, and the more rapid the electrolysis the greater the quantity of hydrogen evolved. Concentrated nitric acid rapidly acts on hydrogen occluded by platinum or palladium, with oxidation of the hydrogen and reduction of the acid. In the electrolysis of concentrated sulphuric acid sulphur is produced, a portion of the hydrogen formed is oxidised and a portion escapes, and the stronger the battery power the greater is the quantity of hydrogen evolved. When the electrolysis is *extremely slow*, no hydrogen is evolved, and sulphur dioxide is produced in small quantity unmixed with free sulphur. Hydrogen occluded by palladium or platinum also reduces sulphuric acid, with production of sulphur dioxide and escape of a portion of the hydrogen.

Gladstone and Tribe regard the metal (platinum or palladium) present in their experiments as instrumental in the chemical change. They think that the hydrogen produced is occluded by the metal and again given off to the acid, and that if the gas is produced more quickly than it can be occluded the excess escapes oxidation by the acid: it is

<sup>1</sup> *C. S. Journal Trans.* for 1879. 178.

<sup>2</sup> *C. S. Journal Trans.* for 1878. 139 and 306.

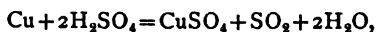


probable, that occluded hydrogen forms a compound with the occluding metal, and that therefore hydrogen coming from this source is for the most part in the nascent, i.e. atomic state. Their experiments certainly establish the fact that maximum reduction of either acid is obtained when hydrogen is evolved therein near an electro-negative metal; but a comparison of the results with occluded and electrolytically evolved hydrogen shews that the reducing action of the latter on sulphuric acid is more complete than that of the former.

The facts, taken as a whole, concerning the action of metals on nitric acid are more in keeping with the hypothesis of the intervention of nascent hydrogen than with the older view, which regarded the various gaseous products as direct results of the deoxidising action of the metal. Indeed to formulate the reaction of zinc on nitric acid on the latter hypothesis, requires that nitric acid should be regarded as a variable compound of nitrogen pentoxide and water, and necessitates considerable skill in the manipulation of formulæ<sup>1</sup>. The action of copper on concentrated sulphuric acid has been studied by Pickering<sup>2</sup>. The ease with which this acid undergoes deoxidation is shewn by the slow production of cuprous sulphide even at 20°; the equation



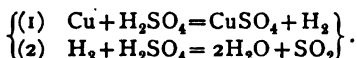
which represents the change as consisting in deoxidation of part of the acid, and does not involve, nor, according to Pickering's experiments allow, an intermediate stage wherein hydrogen reacts on the acid, being nearly realized. At higher temperatures sulphur dioxide is evolved, until at about 270° the action consists entirely of a change which may be formulated as



<sup>1</sup> Deville, *Compt. rend.* 70, 20 & 550; or in abstract, Watts's *Dict. Suppl.* 2, 304. See also Acworth and Armstrong, *C. S. Journal*, vol. 2. for 1877, 54, et seq.

<sup>2</sup> *C. S. Journal Trans.* for 1878. 112.

and which is most readily explained as consisting of two parts proceeding simultaneously



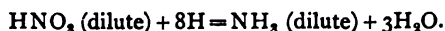
Tin and lead are dissolved by hot concentrated sulphuric acid, with production of sulphates and evolution of hydrogen *and* sulphur dioxide, sometimes accompanied by sulphuretted hydrogen, and with separation of sulphur. With more dilute acid tin evolves hydrogen, and as temperature is increased, sulphuretted hydrogen also. The action of zinc on sulphuric acid is broadly analogous to that of tin.

Quantitative analysis of the products of reduction of nitric acid by magnesium, zinc, and cadmium respectively, shews that reduction is carried furthest by magnesium, and further by zinc than by cadmium. Now the 'heats of formation' (see Chap. IV) of the oxides of these metals are, for Mg 147,132, for Zn 88,244, and for Cd 30,364 thermal gram-units, hence it is almost certain that that reaction of metal on acid in which the greatest amount of heat is evolved is accompanied by the greatest reduction of acid.

The following numbers representing quantities of heat evolved in the chemical changes formulated were obtained by Thomsen (see Chap. IV.).

$\text{H}_2, \text{S}, \text{O}_4, \text{aq.}$	$= 210,760$	gram-units	+
$\text{H}, \text{N}, \text{O}_3, \text{aq.}$	$= 34,270$	"	+
$\text{Zn}, \text{H}_2\text{SO}_4, \text{aq.}$	$= 106,090$	"	+
$\text{Zn}, 2\text{HNO}_3, \text{aq.}$	$= 136,340$	"	+

Berthelot also gives the thermal value of 21,500 gram-units to the chemical change



From these numbers we should expect sulphuric acid to be more stable, towards heat, than nitric acid, and we should expect the action of zinc on these acids to result in a more complete deoxidation of nitric than of sulphuric acid.

In the action of metal on nitric acid at ordinary temperatures, we have then, an unstable acid, a considerable

heat evolution, and the production of hydrogen in contact with the acid, we have conditions eminently favourable to deoxidation. In the action of metal on dilute sulphuric acid, on the other hand, we have a more stable acid and a smaller heat evolution, consequently the hydrogen escapes unchanged; but when the acid is so concentrated that addition of heat from without is required to start the reaction, and when the acid is therefore in a condition more comparable with that of nitric acid at ordinary temperatures, a portion of the hydrogen then evolved undergoes oxidation at the expense of the oxygen of the acid. If however hydrogen is evolved—as in the experiments of Gladstone and Tribe—in contact with concentrated acid at ordinary temperatures, a part of this hydrogen is always oxidised<sup>1</sup>.

The facts, that hot sulphuric acid is deoxidised by carbon, and apparently by phosphorus also<sup>2</sup>, and that it is possible by heat alone to decompose this acid into sulphur dioxide, oxygen, and water, have caused some chemists to regard the actions of metals on this acid as simply cases of direct deoxidation: but it seems to me that the facts enumerated—both chemical and physical, with regard to the action of metals on this acid and on nitric acid—are more in keeping with that hypothesis according to which hydrogen plays an essential part in the series of changes, than with any other hitherto advanced. There may be, indeed there undoubtedly is, more than one process of chemical change resulting in the deoxidation of sulphuric acid, in some cases direct deoxidation preponderates, in others hydrogen plays the more important part.

Experiments recently conducted by Thorpe<sup>3</sup> on the reducing action of zinc, magnesium and tin on acidulated solutions of ferric sulphate, shewed that whatever condition tends to give greater chances of contact between the hydrogen produced in the liquid and the ferric sulphate in solu-

<sup>1</sup> When however vapour of sulphuric acid *mixed with hydrogen* is passed through a hot tube, sulphuretted hydrogen is produced.

<sup>2</sup> Cross, *C. S. Journal Trans.* for 1879. 253.

<sup>3</sup> *C. S. Journal Trans.* for 1882. 289.

tion, increases the rate of reduction; that increase of the rate at which hydrogen is evolved, other conditions remaining constant, is accompanied by decrease of the amount of reduction in unit of time; and that the presence of certain salts, e.g. zinc sulphate, causes a decrease in the rate of reduction. Thorpe's results also established a distinct connection between the nature of the metal used and the influence on the rate of reduction of the varying conditions under which the experiments were conducted.

These experiments, and indeed all experiments on the action of metals on acids, emphasise the necessity that exists for considering all the reacting substances which take part in a process of reduction by hydrogen, and not confining attention to the hydrogen alone. The results of experiments by Tommasi<sup>1</sup> also shew this need: Tommasi found that potassium chlorate was not deoxidised by hydrogen evolved by the action of sodium-amalgam, but was reduced by hydrogen evolved by the action of zinc on diluted sulphuric acid, but that the latter agents failed to remove oxygen from potassium perchlorate.

43. The conception which underlies such expressions as *nascent actions*, *action of nascent hydrogen*, &c., is that implied in the distinction drawn between atom and molecule. That this distinction is one not merely of terminology<sup>1</sup> but based on actual reactions, is rendered apparent by the results of recent experiments by Traube<sup>2</sup> on the conditions under which hydrogen peroxide— $H_2O_2$ —is produced.

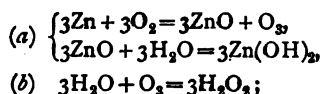
Hydrogen peroxide has been very generally regarded as oxidised water; Traube says it is rather reduced oxygen. The production of hydrogen peroxide during processes of oxidation, occurring in presence of water, has been sought to be explained by assuming that the oxidising substance decomposes oxygen molecules, retains some of the atoms, and sets the others free under conditions favourable to the production of triatomic molecules of ozone, and that the ozone thus produced then reacts on water molecules and con-

<sup>1</sup> See especially *Fogg. Beiblätter*, 2. 205.

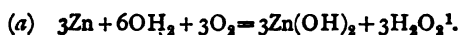
<sup>2</sup> *Ber.* 15. 659, 2421, 2434: 16. 1201.

verts these into molecules of hydrogen peroxide. Traube's hypothesis regards the oxidising substance as decomposing the water molecules present, withdrawing oxygen and part of the hydrogen, and setting free the remainder of the hydrogen, which thereupon combines with oxygen molecules and so produces hydrogen peroxide.

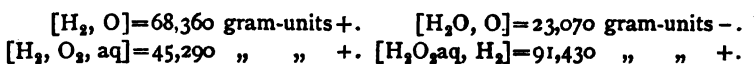
Thus, the production of hydrogen peroxide by the mutual action of zinc, oxygen, and water might be represented, on the first hypothesis, as occurring in two stages,—



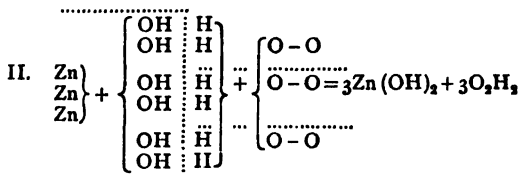
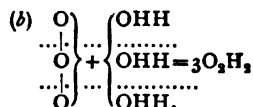
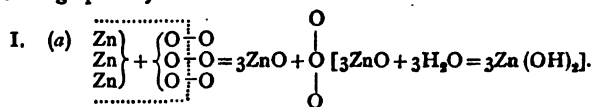
and on the second hypothesis, as occurring essentially in one stage, thus,—



The following numbers, representing the thermal values of various changes, some of which may occur in the complete reaction now under consideration, are taken from Naumann's *Thermochemie*<sup>2</sup>.



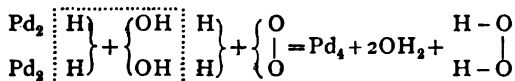
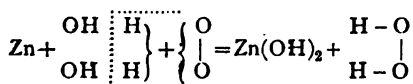
<sup>1</sup> The two hypotheses may be more clearly grasped if these reactions are represented graphically thus:



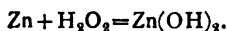
<sup>2</sup> For an explanation of these thermal measurements see *post*, chap. IV., par. 118.

These numbers are opposed to the supposition that water should be readily changed into hydrogen peroxide by a process of direct oxidation. Traube's results, especially those connected with his experiments on electrolysis, seem to shew that neither water nor hydrogen can be directly oxidised to hydrogen peroxide (see pp. 100—101).

Certain metals, e.g. zinc, decompose water only in presence of oxygen, forming hydroxides and hydrogen peroxide; other metals, e.g. sodium, decompose water in absence of oxygen, forming hydroxides and evolving hydrogen; there are other substances, for instance palladium charged with hydrogen, the action of which on water shews that they belong to the same class of substances as zinc. Traube formulates the actions of zinc and hydrogenised palladium (which he regards as a definite compound  $\text{Pd}_2\text{H}$ ) on water in presence of oxygen thus,—

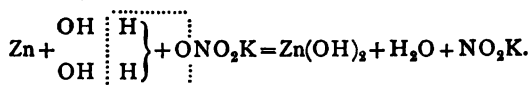


When the quantity of hydrogen peroxide reaches a certain limit a secondary action begins, resulting in the decomposition of the peroxide; thus with zinc,—



Traube thus regards the formation of each molecule of hydrogen peroxide as the result of the action of two atoms of hydrogen on one molecule of oxygen; he does not suppose that the molecule of oxygen is shattered and that its constituent atoms combine with the atoms of hydrogen, but rather that the two hydrogen atoms join themselves on to the already formed oxygen molecule. If this be granted, it seems to follow that, were *atoms* of oxygen presented to the hydrogen atoms as they escape in pairs from the water molecules, water, and not peroxide of hydrogen, would be produced. Traube says that this supposition is shewn to be correct by the reaction of

zinc on an aqueous solution of potassium nitrate; the products of this action are zinc hydroxide, potassium nitrite and water; thus,—



Zinc has no action on an aqueous solution of potassium nitrite, and we know that this salt in the solid form is unchanged at temperatures whereat potassium nitrate parts with one-third of its oxygen.

If the conditions of the preceding action—that viz. of zinc on an aqueous solution of potassium nitrate in presence of oxygen—are arranged so that hydrogen is freely evolved during the change [this can be most readily done by using zinc and iron in place of zinc only], then some of the potassium nitrite is further reduced with production of ammonia. It would appear then that in certain reactions, when hydrogen is separated from water, and oxygen is separated from another compound in contact with the water,—the two gases being brought within the sphere of mutual action in the proportion of two atoms of hydrogen to one atom of oxygen,—water is produced; but that when the hydrogen and oxygen, produced as before, react in the proportion of two atoms of hydrogen to one molecule (not two atoms) of oxygen, hydrogen peroxide is the product.

Traube got some very interesting and important results from experiments on the electrolysis of water, using electrodes of different materials. He found that no hydrogen peroxide was produced when the electrodes were composed of one of those metals which readily produce hydrogen peroxide by their action on water and oxygen (or in some cases dilute acid and oxygen); but that when the electrode consisted of a metal which does not yield hydrogen peroxide under the conditions named, hydrogen peroxide was formed, in greater or less quantity, during electrolysis.

As a typical member of the latter class of metals, Traube chose palladium. When palladium is charged with hydrogen

and made the positive pole of the battery, no hydrogen peroxide is produced, but the oxygen which is being evolved is absorbed by the palladium and is combined with the occluded hydrogen to form water. When however the hydrogenised palladium is made the negative pole, a little hydrogen peroxide is produced; and the quantity of this compound may be considerably increased by causing bubbles of air to rise through the liquid near the negative pole. If however no air is passed through the water, and at the same time the transference of oxygen from the positive pole (where it is being liberated) through the liquid to the negative pole is mechanically prevented, no hydrogen peroxide, or only a trace of this compound, is produced. Further, if hydrogenised palladium is made the positive pole, and bubbles of air are at the same time caused to rise through the liquid around the pole, a little, but only a little, hydrogen peroxide is produced.

Finally if the electrodes are made of palladium uncharged with hydrogen the maximum yield of hydrogen peroxide is obtained (entirely at the negative pole) by arranging the rate of electrolysis so that the whole of the hydrogen produced is occluded by the palladium; the more rapid the evolution of hydrogen from the liquid the smaller is the quantity of hydrogen peroxide produced<sup>1</sup>. Now it is generally supposed that the greater part of the oxygen or hydrogen liberated during electrolysis of water is at the moment of its production in the state of atoms, and that the greater part of the oxygen in ordinary air is composed of molecules; if this be granted, it follows that Traube's experiments establish a marked difference between the reactions of oxygen atoms and oxygen molecules: by their action on hydrogen occluded by palladium, the former produce water, the latter produce hydrogen peroxide; if a few atoms and many molecules of oxygen are present much peroxide and little water are the products, while if many atoms and few molecules of oxygen are brought into contact with the hydrogen, much water and little peroxide is the result.

<sup>1</sup> These results are strictly confirmatory of those obtained by Gladstone and Tribe in their electrolytic experiments on the reduction of acids. See *ante*, p. 93.



44. But the experiments of Traube also shew that the direction and final goal of the chemical change depends not only on the structure of the particles of oxygen, but also on the source and conditions of supply of the hydrogen. If the hydrogen is produced by rapid electrolysis little peroxide is formed; indeed if the hydrogen is produced, rapidly or slowly, by electrolysis with carbon poles no peroxide is obtained. The chemical nature, and the masses, of all the members of the changing system influence the final configuration. The importance of considering the conditions under which hydrogen is produced when we are attempting to explain any of the phenomena classed together as those of nascent state, is emphasised by the fact, already alluded to, that the metals which decompose water in *absence* of oxygen, do not give rise to the production of hydrogen peroxide by their action on water in *presence* of oxygen: for instance, hydrogen peroxide is never produced by the action of sodium on water. It is not enough then that oxygen molecules should be present in contact with atoms of hydrogen as these are liberated from water. The peroxide results from the mutual actions and reactions of the three substances, metal, water, oxygen; if the water is decomposed by the metal alone, hydrogen is evolved rapidly and escapes the pursuit of the oxygen molecules; the peroxide appears to be a product of the joint action of the metal and oxygen on the molecules of water.

This conception of a joint action of metal and oxygen may be carried over to explain some of the phenomena exhibited when metals and acids react. Traube seeks to explain many of these reactions in this way.

Copper does not remove oxygen from an aqueous solution of potassium nitrate as zinc does; but if copper is brought into contact with dilute sulphuric acid in presence of oxygen, hydrogen peroxide is produced. The joint action of copper and potassium nitrate is not sufficient to decompose water-molecules; but copper and oxygen aided by a little sulphuric acid suffice to complete this change. The action in question is represented thus by Traube,—



produced in these reactions; if the action continues for some time no hydroxylamine, but only ammonia can be detected. Addition of hydrochloric or sulphuric acid causes a marked increase in the yield of hydroxylamine. Divers shews that the production of hydroxylamine by the direct action of tin, &c. on nitric acid is most probably preceded by separation of hydrogen from the acid, and that the action of this hydrogen on another portion of the acid is the immediate cause of the formation of hydroxylamine. He also regards his experiments (which it must be admitted are not very numerous) as pointing to the conclusion that the reason why silver, mercury, copper, and bismuth do not produce hydroxylamine or ammonia, when they act on nitric acid, is, that these metals do not displace hydrogen in nitric acid, but rather combine with the nitroxyl and hydroxyl groups, ( $\text{NO}_2$  and  $\text{OH}$ ) forming nitrites and hydroxides ( $\text{MNO}_2$  and  $\text{MOH}$ ), which then mutually react to produce nitrous acid, metallic nitrate, and water. The tin and zinc metals, on the other hand, probably directly produce metallic nitrates, the subsequent formation of nitrites being due to reactions between the metal and its nitrate. Hydroxylamine is an unstable substance; Divers thinks he has experimentally shewn that the increase in the yield of this compound, when nitric and hydrochloric (or sulphuric) acids act on tin, &c. over the yield obtained by the action of nitric acid alone, is chiefly due (1) to production of chloride, or sulphate, of hydroxylamine, both of which salts are more stable than the nitrate, (2) to prevention, by the hydrochloric or sulphuric acid, of formation of nitrous acid, which readily decomposes hydroxylamine, and (3) to production and maintenance of a reducing environment (hydrogen) around the hydroxylamine, by virtue of direct action between the metal and the second acid. Under these circumstances the greater part of the hydroxylamine, produced by the action of the nitric acid on the metal, remains undecomposed. Divers does not find it necessary to suppose that the second acid directly supplies hydrogen for reduction of nitric acid, but, at the same time, he thinks that this reduction is indirectly assisted by the second acid

by virtue of a reaction between it and the metallic nitrate, whereby nitric acid is continually reproduced in the solution. If this is really the case, then it may very well be that formation of hydroxylamine is increased by the simultaneous production, within the sphere of mutual action, of hydrogen and nitric acid, i.e. by the presence in the solution of *nascent* hydrogen and *nascent* nitric acid. The nature of the second acid, as might be expected, is an important factor in the change: the amount of water present, and the temperature at various stages of the reaction also exert marked influence on the final result.

45. The expression 'nascent action' has probably been at once helpful and harmful to the progress of chemistry. By classing under a common name many phenomena that might otherwise have been lost in the vast mass of facts with which the science has to deal, the expression has, I think, done good service; but in so far as its use has tended to prevent investigation—for it is always easier to say of any unusual reactions, 'these are cases of nascent action' than to examine carefully into their course and conditions—and also in so far as it has favoured the impression that 'nascent' hydrogen or 'nascent' oxygen, &c. is ordinary hydrogen or oxygen, &c. with certain indefinite properties which are always attached to the hydrogen, or other element, when in this peculiar condition, the use of the expression has, I think, been unfavourable to the best interests of chemical science.

A study of the reactions in which nascent substances play important parts appears to me to keep before the student that all-important distinction between the atom and the molecule which is so vital in chemical considerations, and also to draw attention in a marked way to the complexity of all chemical changes. We find, or think we find, that when atoms of hydrogen are presented to another substance in a given chemical reaction, certain definite products result; and we are apt to conclude that the action of hydrogen atoms on this substance will always give this result; but investigation discovers that not only the course of the reaction, but also the final configuration of the changing system, is dependent on

the whole previous history of the reacting bodies. Hydrogen as it is produced by the action of sodium-amalgam appears to possess properties different from those which characterise hydrogen produced by the action of zinc on dilute sulphuric acid; attempts to explain these apparent differences lead to fresh researches; we become impressed with the conviction that chemistry is not the study of this element or that, regarded as a kind of matter with certain fixed physical properties, but that processes of change are the subject-matter of the science, and that to explain any one of these we must take into account each and all of the reacting bodies, and each and all of the conditions under which the total change is proceeding.

If the expression 'nascent action' does in any way help to emphasise such considerations as these, I think it ought to be retained in chemical nomenclature.

## SECTION II. *The Dualistic and Unitary Theories.*

46. Partly from his definition of element, partly from his study of the products of combustion in oxygen, of phosphorus, carbon, sulphur, &c., Lavoisier was led to regard every salt as formed by the union of an acid with a radicle, the latter being itself either simple or compound.

Davy began his electro-chemical researches in the early years of the present century. In the *Philosophical Transactions* for 1807<sup>1</sup>, and in his *Elements of Chemical Philosophy*<sup>2</sup>, he regards chemical combination as accompanied by an exchange of quantities of electricity of opposite sign between the combining bodies. He found that when sulphur and copper are rubbed together the sulphur is negatively, the copper positively, electrified; and that when the sulphur is heated the electrical activities become more apparent, until the sulphur melts, when chemical combination occurs and the product, copper sulphide, exhibits neither positive or

<sup>1</sup> 'On some chemical agencies of electricity,' p. 1.

<sup>2</sup> *Collected works*, vol. IV. (see also Ladenburg's *Entwicklungsgeschichte der Chemie*, pp. 75—81).

negative electricity. If the quantity of electricity lost in the act of chemical union is restored, e.g. by the passage of a current through the compound formed, chemical decomposition occurs and the original components are again obtained. Davy regarded the primary cause of chemical and electrical effects as possibly the same force; when this force is exerted between masses of matter electrical phenomena result; when it is exerted between the smallest particles of bodies chemical phenomena result. Thus in his *Elements of Chemical Philosophy*<sup>1</sup> Davy says, 'Electrical effects are exhibited by the same bodies when acting as masses, which produce chemical phenomena when acting by their particles; it is not therefore improbable that the primary cause of both may be the same, and that the same arrangements of matter, or the same attracting powers, which place bodies in the relations of positive and negative, i.e. which render them attractive of each other electrically, and capable of communicating attractive powers to other matter, may likewise render their particles attractive, and enable them to combine, when they have full freedom of motion.' 'That the decomposition of the chemical agents is connected with the energies of the pile, is evident from all the experiments that have been made; as yet no sound objection has been urged against the theory that the contact of the metals destroys the electrical equilibrium, and that the chemical changes restore it; and, in consequence, that the action exists as long as the decompositions continue<sup>2</sup>.'

47. At once a brilliant theoriser and a thorough-going experimenter, Davy did not attempt to found a general scheme of chemical classification on his electro-chemical work. This was however done by Berzelius, who developed a consistent and definite, although narrow theory which for a time seemed to explain all chemical phenomena.

<sup>1</sup> *Loc. cit.* pp. 119—120, and p. 125.

<sup>2</sup> It is interesting to observe how similar this view, stated by Davy in the beginning of the present century, is to the latest views regarding the connection of chemical and electrical forces. Compare especially Helmholtz's 'Faraday Lecture.' (*C. S. Journal Trans.* for 1881, 277 *et seq.*: see particularly pp. 300—302.) [See *post*, Book II.]

All chemical actions were regarded by Berzelius as brought about by electrical force<sup>1</sup>. '*Die Elektrizität...scheint die erste Thätigkeits-Ursache in der ganzen, uns umgebenden Natur zu sein.*' Electrical actions, according to Berzelius, were not to be described as consequences of contact, or of mutual action between heterogeneous bodies. Each elementary atom, he held, is endowed with two kinds of electricity, it has two electric poles; but these poles differ in strength, so that each atom considered as a whole is characterised as positively *or* negatively electrified; in some elementary atoms positive electricity predominates and gives a positive character to the whole atom; in others negative electricity overpowers the positive. When a positively electrified atom attracts a negatively electrified atom, opposite electricities neutralise one another, but the electricities formerly masked in the separate atoms now come into play, and so the new group of atoms, as a whole, exhibits positive or negative electricity, in virtue of which it is capable of chemically combining with other atoms or groups of atoms. But as the stronger poles are first neutralised, it follows that the more complex a compound is, the less polarity does it exhibit, and hence the less readily does it combine with other substances. Berzelius moreover regarded the quantity of electricity on either pole as to some extent variable with variations of temperature. On the Berzelian theory atoms are regarded as essentially unipolar; one polarity so predominates over the other that each atom acts as a positively *or* negatively electrified whole.

The electro-chemical properties of oxidised compounds, Berzelius taught, depend chiefly on the unipolarity of the electro-positive radicles they contain. Of two oxides, that which contains the more electro-negative radicle is generally itself electro-negative; thus sulphuric acid (regarded as  $\text{SO}_2$ ) is electro-negative to all metallic oxides, because sulphur is itself electro-negative to all metals; on the other hand the oxides of potassium and sodium are electro-positive to all other oxides (excepting those of cæsium and rubidium) be-

<sup>1</sup> *Lehrbuch* (1st Ed.), III. part I. p. 77.

cause potassium and sodium are themselves electro-positive to all other elements<sup>1</sup> (except cæsium and rubidium).

Polarity and chemical affinity are closely connected in the system of Berzelius: the 'specific unipolarity'<sup>2</sup> however does not alone determine the greater or less affinity of one atom for another. Some atoms have a more intense polarity than others and therefore exhibit a greater striving ('*Bestreben*') to neutralise the electricity divided between their poles, in other words, have a greater affinity for a given substance than other atoms.

Chemical affinity appears to have been regarded by Berzelius as nearly synonymous with intensity of atomic polarity<sup>3</sup>. Thus, oxygen combines with sulphur rather than with lead, although oxygen and sulphur have the same unipolarity (viz. negative); but, the Berzelian view asserts, the positive pole of the sulphur atom neutralises more negative electricity on the oxygen atom than can be neutralised by the positive pole of the lead atom.

Double decompositions were readily explained in terms of this theory: 'Every chemical action,' says Berzelius<sup>4</sup>, 'is an electrical phenomenon depending on the electrical polarity of the particles; everything that appears to be due to the action of affinity is caused by the possession by some bodies of an electrical polarity stronger than that of others. If the compound *AB* is decomposed by the substance *C* which has a greater affinity for *A* than *B* has, then *C* must possess a more intense electrical polarity than *B*; on this account there results more complete neutralisation between *A* and *C* than between *A* and *B*.... If two bodies, *AB* and *CD*, so

<sup>1</sup> An important deduction made from these considerations is, that as oxygen occurs both in markedly electro-positive and electro-negative compounds, and as acids are as a group electro-negative, oxygen cannot be the acidifying element, as Lavoisier said it was.

<sup>2</sup> *Specifische Unipolarität*. Berzelius, *loc. cit.* p. 73.

<sup>3</sup> This might perhaps be regarded as equivalent to the modern conception of higher and lower potential; as if one atom might have a smaller electrical charge but at a higher potential than another, and would therefore exhibit greater chemical affinity than the other.

<sup>4</sup> *Lehrbuch* (1st Ed.), III. part I. p. 77.



'react as to produce two new bodies, *AD* and *BC*, it follows that the electrical polarities are better neutralised in the latter pair of bodies than in the former.'

48. On the basis of this theory Berzelius raised the structure of the dualistic chemistry, which asserted that every compound, whether simple or complex, must be constituted of two parts, of which one is positively, and the other negatively electrified.

The doctrine of dualism is thus introduced by Berzelius<sup>1</sup>: 'If these electro-chemical conceptions are just, it follows that every chemical compound is dependent on two opposing forces, positive and negative electricity, and on these alone; and that every compound must be composed of two parts held together by their mutual electro-chemical reactions. Therefore it follows that every compound body, whatever be the number of its constituents, can be separated into two parts, whereof one is positively and the other negatively electrified. Thus, for example, sodium sulphate is put together, not from sulphur, oxygen, and sodium, but from sulphuric acid and soda, which again can themselves be separated into positive and negative constituents. So also alum cannot be regarded as immediately built up from its elements, but must rather be looked on as the product of a reaction between sulphate of alumina and sulphate of potash, the former acting as a negative, the latter as a positive element.'

In support of his theory Berzelius appealed to the facts of electrolysis. A solution of sodium sulphate containing a little blue vegetable colouring matter is electrolysed; the colouring matter is reddened around the positive electrode and rendered more distinctly blue around the negative. What can this experiment teach but that the salt is separated by the electric current into alkali and acid? And can the inference be avoided that the salt is composed of, or contains in itself,

<sup>1</sup> *Lehrbuch*, loc. cit. p. 79.

<sup>2</sup> See also Berzelius, *Theorie des proportions chimiques, et de l'influence chimique de l'électricité dans la nature inorganique*; 3rd Ed. Paris, 1835. Also, for a condensed account of the electro-chemical theory of Berzelius, see Ladenburg, loc. cit. pp. 89-93.

these two compound radicles, soda ( $\text{Na}_2\text{O}$ ) and sulphuric acid ( $\text{SO}_3$ )? All salts were to be regarded as dualistic structures. Given the composition of a salt, a dualistic formula—or rather a series of formulæ—was at once devised for it. The following formulæ were employed by various dualistic chemists to express the structure of acetic acid,—

- |   |   |  |
|---|---|--|
| (1) $\text{C}_4\text{H}_6\text{O}_3 \cdot \text{H}_2\text{O}$             | (2) $\text{C}_4\text{H}_6\text{O}_4 \cdot \text{H}_2$             | (3) $\text{C}_4\text{H}_6\text{O} \cdot \text{O}_2 \cdot \text{H}_2\text{O}$ |
| (4) $(\text{C}_2\text{H}_4)\text{C}_2\text{O}_3 \cdot \text{H}_2\text{O}$ | (5) $(\text{C}_2\text{H}_4)\text{C}_2\text{O}_4 \cdot \text{H}_2$ | (6) $(\text{C}_3\text{H}_6\text{O})\text{CO}_2 \cdot \text{H}_2\text{O}$     |
| (7) $\text{C}_4\text{H}_8 \cdot \text{O}_4$                               | (8) $\text{C}_2\text{H}_4 \cdot \text{O}_2$                       | (9) $\text{C}_4\text{H}_6\text{O}_2 \cdot \text{H}_2\text{O}_2$              |
| (10) $\text{C}_4\text{H}_2 \cdot \text{O}_4\text{H}_6$                    |   |  |

To choose the proper formula from such a chaos was a task possible only for one whose foible was omniscience. That formula which had the weight of authority on its side was accepted as correct.

49. Lavoisier had regarded oxygen as the ‘acidifying principle’. Hydrochloric acid was undoubtedly an acid substance, therefore, in accordance with the dictum of Lavoisier, it contained oxygen. Davy’s study of this compound, and of its analogue hydriodic acid, nevertheless established the fact that an acid can exist which contains no oxygen. The further fact, that so many of the oxides—then called acids—exhibited acid properties only in presence of water, led Davy to the belief that very many acids contain hydrogen. Shaking off the trammels of that older philosophy which regarded the introduction of undefined ‘*principles*’ as affording explanations of natural phenomena, Davy said that acids are not characterised by the invariable presence of any one element, but that certain compounds of very diverse elements belong to this group<sup>1</sup>.

Dulong<sup>2</sup> in 1815 further advanced Davy’s conception of acids by recognising no essential difference between those acids which contain oxygen and those which do not. Lavoisier’s acid theory was not however generally abandoned until many years later.

<sup>1</sup> For an account of the important work of Davy on the non-oxygenised acids, and the arguments of his opponents, see Ladenburg, *loc. cit.* pp. 81–87.

<sup>2</sup> *Mem. de l’Acad.* 1813–15, p. 198, and *Schweigger’s Journal*, 17. 229.

In 1837—38 Liebig<sup>1</sup>, following up Graham's work on phosphoric acid<sup>2</sup>, distinctly recognised the existence of 'replaceable hydrogen' in acids, whether oxy-acids or acids containing no oxygen, and defined salts, as compounds belonging to the same class as acids, and formed by putting metal in place of an equivalent quantity of hydrogen in acids<sup>3</sup>.

This view of the structure of salts was altogether opposed to the dualistic theory of Berzelius.

50. Another severe blow was inflicted on the prevailing theory by Faraday's researches on electrolytic decompositions.

Faraday shewed that the quantities of various elements set free from different electrolytes, by the same electric current, were chemically equivalent to one another: thus for each two parts by weight of hydrogen set free from water, there were obtained 16 parts of oxygen, 78·2 parts of potassium, 63·5 parts of copper from persalts and 127 parts of copper from protosalts. But the affinities of the atoms of the various electrolytes were undoubtedly different in each combination. According to Berzelius, the quantity of electricity collected on any group of atoms is greater, the greater the mutual affinity of these atoms; but Faraday's experiments shewed, that in so far as this electricity was measurable by electrolytic decomposition, (and that at least comparative measurements should be thus obtained followed from the terms of the dualistic theory itself), the quantity of it was in no way dependent on the affinities of the combining atoms<sup>4</sup>.

51. A bold and partially successful attempt—such an attempt as could be made only by a man of preeminent power—had been made by Berzelius to found chemical classification on the study of composition alone, almost wholly divorced from the study of function, or power of doing.

<sup>1</sup> *Compt. rend.* 5. 863 (with Dumas): and *Annalen*, 26. 113, see especially p. 181.

<sup>2</sup> *Phil. Trans.* for 1833. 253.

<sup>3</sup> See, in connection with *acid* generally, Laurent, *Chemical Method*, pp. 39—45.

<sup>4</sup> See Helmholtz, 'The Faraday Lecture.' *C. S. Journal Trans.* for 1881. pp. 284—6.

As his authority became greater, Berzelius led chemistry further from the only true path by which she could advance, that namely wherein experiment, and reasoning on experimental data, go hand in hand. And yet no single chemist has enriched the science by the addition of so great a mass of laboriously and accurately determined experimental data as he. The intense concentration of his great intellectual powers upon one view of chemical phenomena led Berzelius to disparage the reasoning of those who sought to view these phenomena from standpoints other than his own.

Among those who recalled chemistry to the true scientific method, Dumas, Laurent, and Gerhardt stand pre-eminent.

In 1839<sup>1</sup> Dumas described trichloroacetic acid, obtained by the action of chlorine on acetic acid. The new compound, although containing chlorine in place of hydrogen, was a monobasic acid, and resembled acetic acid in its general reactions. Dumas said there are certain *types* in organic chemistry which are maintained even when an equal volume of chlorine, bromine, or iodine, is put in the place of hydrogen in the parent substance<sup>2</sup>.

Berzelius, and the defenders of the dualistic chemistry, violently opposed the idea that the electrically negative chlorine could be substituted for the positive hydrogen, and the identity of type yet be maintained. In Dumas' succeeding papers<sup>3</sup> the conception of types was more fully developed. All bodies containing the same number of equivalents of simple substances, combined in a similar manner, and exhibiting broad analogies of properties, were regarded as belonging to the same type. Such bodies were also, as a rule, simply related to one another by reactions of formation and decomposition:—thus acetic and chloroacetic acids; chloroform, bromoform, and iodoform; ethylene and its chloro-

<sup>1</sup> *Compt. rend.* 8. 609, and *Annalen*, 32. 101.

<sup>2</sup> *Compt. rend.* 8. 621.

<sup>3</sup> *Annalen*, 33. 259; 35. 129 (with Stas), and 289 (with Peligot); or *Compt. rend.* 9. 813, and 10. 149.

derivatives, &c., belonged to the same types, or as Dumas said to the same 'natural families'. Dumas regarded carbonyl chloride as derived from carbonic anhydride by substituting one oxygen by two chlorine atoms—thus  $\text{COO}$  gives  $\text{COCl}_2$ ; this was utterly opposed to the dualistic view, according to which the formula of carbonyl chloride was written  $\text{CO}.\text{CCl}_2$ , because every compound *must* be composed of two parts, one of which is electrically positive and the other negative.

52. The new school of chemists naturally opposed the conception of compound radicles, a conception too closely associated with those dualistic theories they were leaving behind, to find favour in their sight. But these chemists found that unless substitution of simple atoms by groups of atoms were regarded as possible, identity of type could not be maintained through groups of compounds undoubtedly belonging to the same natural family.

Inasmuch as the new chemistry based its claims to recognition on an appeal to actual reactions, it was impossible that it should long refuse to recognise the conception of compound, as well as simple, radicles, without proving false to its own method. Liebig and Wöhler, in their researches on oil of bitter almonds, explained the observed reactions of the compounds they obtained by assuming the existence of the compound radicle *benzoyl* ( $= \text{C}_{14}\text{H}_{10}\text{O}_2$ ) in these bodies (see *Annalen*, 3, 249).

But what are these compound radicles which the chemists who upheld the unitary system were obliged to recognise, equally with their opponents who supported a dualistic theory? Are they definite groups of atoms always existing as such in compound molecules, or are they only convenient methods of expressing and generalising reactions?

As chemistry advanced, compound radicles came to be generally recognised as certain groups of atoms, in compound molecules, which remain undecomposed throughout a series of reactions undergone by those compounds<sup>1</sup>. Thus

<sup>1</sup> See especially Laurent's *Chemical Method*, pp. 276—300. Also Ladenburg, *loc. cit.* 9th and 10th Lectures.

we find Kekulé in 1857 citing the case of sulphuric acid,  $\text{H}_2\text{SO}_4$ , which when acted on by zinc gives  $\text{ZnSO}_4$ , and may therefore be said to contain the radicle  $\text{SO}_4$ , but when acted on by phosphorus pentachloride, the compound  $\text{SO}_2\text{Cl}_2$  is produced, hence the acid may be said to contain the radicle  $\text{SO}_2$ <sup>1</sup>.

53. The conception of types was destined to bear much fruit. Let us briefly trace its development.

Liebig and Dumas had regarded salts as substituted metallic derivatives of acids, they had spoken of a quantity of metal as taking the place of an equivalent quantity of hydrogen; Dumas had even ventured to regard the negative chlorine as capable of replacing an equivalent amount of the positive hydrogen. In doing this, these chemists had returned to the old conception of equivalents—too much forgotten by the Berzelian school—as quantities to be determined by the study of reactions, but they had given this conception fresh life by engrafting on to it the notion of natural families or types.

In writing the formulæ of sulphates, selenates and chromates, as  $\text{MO} \cdot \text{SO}_3$ ;  $\text{MO} \cdot \text{SeO}_3$ ; and  $\text{MO} \cdot \text{CrO}_3$ , Berzelius had undoubtedly recognised the principle of types; but so long as this principle was dominated by the necessities of the dualistic system it was unfruitful. The idea of the chemically reacting unit as one whole, one structure with parts capable of replacement by other parts without the necessary destruction of the building, gave meaning to what was before but a form of words.

From its earliest beginnings to its present form the theory of types has been interwoven with the atomic theory; without the latter, the former had never had being. If the value of a scientific idea is to be measured by its fruitfulness, then is Dalton's *New System of Chemical Philosophy* the most important work yet produced by any chemist.

Now if the reacting unit of any substance is possessed of a definite atomic structure, only those bodies can be said

<sup>1</sup> The modern development of the conception of compound radicle will be better understood by considering pars. 70 to 74 in Section 4 of this chapter.

to belong to the same type, or natural family, whose reacting units are built on a similar atomic plan: but our only method of discovering similarity of structure is by studying reactions; hence only those bodies which are characterised by similarity of chemical function ought to be classified under the same type<sup>1</sup>. And as modification of structure has been recognised as not necessarily implying destruction of type, it follows that those quantities of radicals, simple or compound, are equivalent, which can perform similar functions in similarly constituted compounds.

At last a method of chemical classification has been found by Dumas, Liebig, Gerhardt, and Laurent which, when more fully developed, will reconcile those who regard composition as all important, with those for whom function is supreme; which will preserve the fundamental conception of equivalent, but interpret it in terms of the wider theory of atoms; and which will recognise the connection, while yet emphasising the importance of the difference between the atom of Dalton and the molecule of Avogadro.

But in its development the theory of types must necessarily be largely modified. Classification by types cannot be final in a science which has advanced so far towards becoming an abstract science as chemistry.

‘By the classification of any series of objects is meant ‘the actual, or ideal, arrangement together of those which ‘are like and the separation of those which are unlike; the ‘purpose of this arrangement being, primarily, to disclose the ‘correlations or laws of union of properties or circumstances, ‘and, secondarily, to facilitate the operations of the mind ‘in clearly conceiving and retaining in the memory the “character of the objects in question”.’

Those ‘properties or circumstances’ which are correlated must be such as are really characteristic of the objects classified, they must be essential properties of these objects, not mere surface appearances; they must be capable of accurate

<sup>1</sup> See especially Laurent’s *Chemical Method*, pp. 298—300.

<sup>2</sup> W. Stanley Jevons (modifying the words of Huxley), *Principles of Science*, 2. p. 348.

definition, and at the same time of fairly easy recognition; and that property—or properties—chosen as the mark of a class must belong to all the members of that class.

But the properties of a type are necessarily somewhat vague: properties regarded by one observer as essentially belonging to the type may by another be regarded as accidental; a given substance may possess so many of the properties of the type as at one time suffices to ensure its admission into the class, but at a future time new properties may be discovered which necessitate the removal of the substance to a class whose type shews considerable divergence from that under which the substance was originally placed.

The very elasticity, and even vagueness, of the theory of types ensured it an important place in the development of chemical science.

### SECTION III. *Equivalency of atoms.*

54. Dualism had reigned supreme, but only because it was despotic; when the rebellion, headed by Dumas, once got a footing the fate of the older theory was sealed. The new system succeeded because it was not too systematic.

In attempting to preserve unity of type through large series of compounds, the builders of modern chemistry were obliged to make free use of the conception of compound radicles as substituting simple radicles; they thus became familiarised with the general notion of each radicle possessing a definite substituting power.

In 1852 Frankland<sup>1</sup> extended this conception to the atoms of the elementary bodies; in 1855 Odling<sup>2</sup> introduced the use of dashes placed over the atomic symbols to express what he called 'the replaceable, or representative, or substitu-

<sup>1</sup> *Phil. Trans.* 142. 417, see especially p. 440.

<sup>2</sup> *C. S. Journal*, 7. 1. (The recognition of two 'replaceable values' for the iron atom, and other atoms, shews the close connection between the theory then coming into existence and the older theory of equivalents.)



'tion value' of these atoms, he also recognised that an elementary atom may have more than one 'replaceable value'. Odling applied this fruitful conception to the formulæ of many salts, especially the phosphates, and succeeded in shewing analogies until then overlooked.

The inherent fascination of the idea of compound radicle may be realised, by considering that in less than twenty years after Dumas' discovery of the chloracetic acids—which marks the beginning of the revolt against the compound radicles of dualism—Kekulé<sup>1</sup>, and independently of him, Couper<sup>2</sup> (in papers of the greatest importance) found it necessary to recall chemists to the consideration of elementary atoms as being the true units by the combinations of which all compound molecules are built up, and by whose properties those of the compounds are determined. Couper criticised Gerhardt's development of types, objecting to the vagueness of the idea as a basis for classification; and especially opposing Gerhardt's opinion that the molecular constitution of bodies can never be ascertained by chemists. 'Would 'it not be rational,' says Couper, 'in accepting this veto to 'renounce chemical research altogether?' This dictum of Gerhardt is to be traced, in Couper's opinion, to the overdue employment of compound radicles, to forgetting that these can have no properties which are not 'a direct consequence of 'the properties of the individual elements of which they are 'made up,' and hence to endowing these radicles with some 'unknown and ultimate power which it is impossible to 'explain.' Returning then to a study of the elements, Couper finds chemical affinity as a property inherent in, and common to them all; he distinguishes 'affinity of kind' and 'affinity 'of degree;' applying the latter to carbon, he cites the oxides CO and CO<sub>2</sub> (in his notation C<sub>2</sub>O<sub>2</sub> and C<sub>2</sub>O<sub>4</sub>), the former expressing the first, the latter the second and last degree: CO<sub>2</sub> is 'the ultimate affinity, or combining unit 'for carbon.'

<sup>1</sup> *Annalen* (1857), 104. 129.

<sup>2</sup> *Phil. Mag.* (1858) [4], 16. 104.

Kekulé in 1857, and more especially in a paper published in March 1858<sup>1</sup>—a paper the importance of which can hardly be overrated—distinguishes more clearly than Couper ‘affinity of kind’ from ‘affinity of degree;’ or rather he distinguishes chemical affinity from what he calls the ‘*basicity of atoms*,’ both conceptions being needed, he says, for the explanation of chemical combinations. Kekulé clearly distinguishes—and this distinction has been too much forgotten in recent developments of chemical theory—between equivalent weights of elements, and equivalency (or basicity) of elementary atoms; he shews that the new theory deals with definite entities, called atoms, having defined properties, and not with ‘unit weights,’ and that it is these atoms which he proposes to compare as to their substituting power for the hydrogen atom. Having shewn that one atom of carbon, so far as our knowledge goes, is never combined with more than four atoms of hydrogen in a compound molecule, Kekulé also shews that two atoms of carbon do not bind to themselves more than six atoms of hydrogen, three atoms of carbon not more than eight atoms of hydrogen, and so on.

The *tetravalency* of the carbon atom, and the power which two, or more, atoms of carbon possess of binding themselves together in a molecule, are enunciated by Kekulé in this paper, which forms the foundation stone of the modern theory of ‘atom-linking’<sup>2</sup>.

Kekulé and Couper insisted, that if a definite theory of the connections between properties and structure of compounds is to be obtained, it must be based on the study of the combining powers of the elementary atoms: ‘The whole is simply a derivative of its parts,’ said Couper.

55. A theory which shall attempt to explain the atomic structure of compound molecules, must, in the present state

<sup>1</sup> *Annalen*, 106. 129.

<sup>2</sup> In comparing Couper’s paper with Kekulé’s it may be well to notice how Couper attempts to trace a close connection between the *basicity of atoms* and chemical affinity; his statements are here much vaguer than Kekulé’s, yet this dynamical method of regarding ‘valency’ at the very outset of the theory is important.

of knowledge, confine itself to gaseous bodies. We do not know how to determine the relative weights of the molecules of solid or liquid substances. We have reason to believe that the molecular structure of a mass of solid or liquid is much more complex than that of a mass of a gaseous substance; no generalisations have yet been made regarding molecular phenomena of solids or liquids comparable with those which—under the names of the laws of Boyle, Charles, and Avogadro—have been made regarding molecular phenomena of gases. We must recognise the limits within which a theory of atomic structure can assist advance; if it be pushed too far it will become, with some a dogma, with others a thing to be scorned.

Considering these molecular formulæ  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{H}_3\text{N}$ ,  $\text{H}_4\text{Si}$ , it is seen that one atom of chlorine is combined with one atom of hydrogen in the molecule  $\text{HCl}$ , that one atom of oxygen is combined with two atoms of hydrogen in the molecule  $\text{H}_2\text{O}$ , that one atom of nitrogen is combined with three atoms of hydrogen in the molecule  $\text{H}_3\text{N}$ , and that one atom of silicon is combined with four atoms of hydrogen in the molecule  $\text{H}_4\text{Si}$ . Considering the molecular formulæ  $\text{ClH}$ ,  $\text{Cl}_2\text{Hg}$ ,  $\text{Cl}_3\text{Bi}$ , and  $\text{Cl}_4\text{Sn}$ , it is seen that one atom of hydrogen is combined with one atom of chlorine, one atom of mercury with two atoms of chlorine, one atom of bismuth with three atoms of chlorine, and one atom of tin with four atoms of chlorine, in various compound molecules.

These facts may be expressed by saying that the atoms of oxygen and mercury are *divalent*, the atoms of nitrogen and bismuth are *trivalent*, and the atoms of silicon and tin are *tetravalent*, i.e. so far as the data at present before us are concerned, the atom of oxygen or of mercury can combine with two atoms of hydrogen or of chlorine, the atoms of nitrogen and bismuth can combine with three atoms of hydrogen or chlorine, &c., to form compound molecules.

56. But these terms *monovalent*, *divalent*, &c., must be more strictly defined.

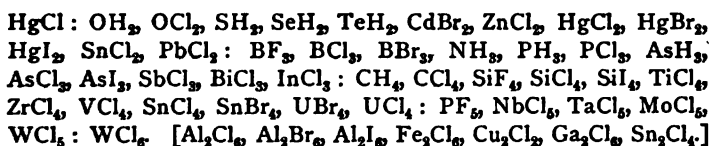
If the table on pp. 37—40 is examined, it will be found that all molecules of gases containing only atoms of *hydrogen*,

[fluorine]<sup>1</sup>, chlorine, bromine, iodine<sup>2</sup>, and thallium, contain two atoms; the molecules in question are,—



These then—H, [F]<sup>1</sup>, Cl, Br, I, Tl—are monovalent atoms, i. e. atoms which combine each with one other atom to form molecules.

Now if we tabulate the formulæ of molecules composed of two elements, one of which is H, F, Cl, Br, I, or Tl, we have this result,—



Omitting the formulæ in brackets,—inasmuch as these molecules contain more than a single atom of the element other than H, F, Cl, Br, I, or Tl,—the following arrangement expresses the results of this tabulation.

*Monovalent atoms H, F, Cl, Br, I, Tl.*

- |      |  |                                       |
|------|--|---------------------------------------|
| I.   | Atoms which combine with one monovalent atom to form a compound molecule | Hg.                                   |
| II.  | Do. two  | do. O, S, Se, Te, Cd, Zn, Hg, Sn, Pb. |
| III. | Do. three  | do. B, N, P, As, Sb, Bi, In.          |
| IV.  | Do. four   | do. C, Si, Ti, Zr, V, Sn, U.          |
| V.   | Do. five   | do. P, Nb, Ta, Mo, W.                 |
| VI.  | Do. six  | do. W.                                |

When it is said that one atom is combined with another, direct action and reaction between these atoms in the molecule is assumed. In saying, therefore, that one bismuth atom

<sup>1</sup> Mallet [*Amer. Chem. Journal* 3. 189] has shewn that at low temperatures the molecule of hydrofluoric acid must be represented by the formula  $\text{H}_2\text{F}_2$ ; at higher temperatures however the formula HF represents the molecule of this gas. It is possible that hydrofluoric acid is a 'molecular compound' at low temperatures (see Section 5 of the present chapter); determinations of the density of this gas for a considerable range of temperature would throw light on this question.

<sup>2</sup> The iodine molecule is probably monatomic at very high temperatures, and so forms an exception to this statement. (See *ante*, p. 42, par. 20.)

is combined with three chlorine atoms in the molecule  $\text{BiCl}_3$ , it is assumed that the bismuth atom acts directly upon (and is acted on by) each chlorine atom. This is not proved by the formula  $\text{BiCl}_3$ : it might be assumed that the bismuth atom acts indirectly on one chlorine atom through another chlorine atom; but, considering that all molecules which contain a single atom of chlorine contain only one other atom, the simplest hypothesis is that the bismuth atom is trivalent in the molecule  $\text{BiCl}_3$ .

57. A monovalent atom has been defined to be an atom which combines with one other atom to form a molecule. The best definition of a di-, tri-, &c.-valent atom would probably be,—an atom which combines with two, three, &c. other atoms to form a molecule<sup>1</sup>; but the definition generally adopted is,—an atom which combines with two, three, &c. *monovalent* atoms to form a molecule.

According to this definition the valency (or equivalency, or quantivalence) of an elementary atom is a number which tells the number of monovalent atoms (i.e. atoms of H, F, Cl, Br, I, or Tl) with which the given atom combines to form a molecule. Of the 26 elements (not including, that is, the typical monovalent atoms) in the foregoing six series, four, viz. P, Sn, W and Hg, are found each in two series. Recalling the fact that an element has frequently more than one equivalent number, and remembering that we are now endeavouring to arrange the elementary atoms in groups, the members of each of which are to be equivalent among themselves, this variation in the valency of the atoms of these four elements is not surprising.

The fact that the number of monovalent atoms combining with some of the other elementary atoms is variable, necessitates an addition to the definition of valency, which may now run thus. *The valency of an elementary atom is a number which tells the maximum number of monovalent atoms (i.e.*

<sup>1</sup> In Frankland's paper already referred to [*Phil. Trans.* 142. 417.] this definition is apparently adopted, 'no matter what the character of the uniting atoms may be, the combining power of the attracting element.....is always satisfied by the same number of these atoms' (p. 440).

*atoms of H, F, Cl, Br, I, or Tl) with which the given atom combines to form a molecule.* Of the four atoms in the arrangement on p. 121 whose valency is expressed by more than one number, two,—mercury and tungsten,—combine with an odd or an even number of monovalent atoms, one,—tin,—combines with an even number only, and one,—phosphorus,—combines with an odd number only, of monovalent atoms, to form compound molecules.

If those molecules which contain only H, F, Cl, Br, I, or Tl atoms and the group of atoms methyl ( $\text{CH}_3$ ) or ethyl ( $\text{C}_2\text{H}_5$ ) are tabulated<sup>1</sup>, it is found that such molecules contain two atoms, that is if it be permitted to apply the term 'atom' to the group ( $\text{CH}_3$ ) or ( $\text{C}_2\text{H}_5$ ). These groups may therefore be regarded as monovalent. By tabulating the formulæ of molecules composed of two 'elements,' one of which is methyl or ethyl, we find that lead is to be added to the list of those elements the valency of whose atoms varies but is always expressed by an even number<sup>2</sup>.

Molecules which do not contain monovalent atoms cannot be employed for decisively fixing the valencies of atoms, although arguments for or against a certain valency may be drawn from consideration of such molecules.

58. From the data already given, the oxygen atom is said to be divalent: now it might be argued that if a molecule is found containing one atom of oxygen and one atom of another element, the second atom is divalent; if a molecule is found containing two atoms of oxygen and one atom of another element, the second atom is tetravalent, &c. The molecules CO and  $\text{CO}_2$  are cases in point. The latter ( $\text{CO}_2$ ) has been often used—e.g. by Kekulé in his paper of 1858—to prove the tetravalency of the carbon atom. Let the valency of an atom be represented by one, two or more straight lines proceeding from the atomic symbol, thus H—, —O—, —Bi—, &c., then the formula  $\text{O}=\underset{\textstyle |}{\text{C}}=\text{O}$  expresses.

<sup>1</sup> These molecules are  $(\text{CH}_3)_2\text{H}$ ,  $(\text{CH}_3)_2\text{F}$ ,  $(\text{CH}_3)_2\text{Cl}$ ,  $(\text{CH}_3)_2\text{Br}$ ,  $(\text{CH}_3)_2\text{I}$ ,  $(\text{C}_2\text{H}_5)_2\text{H}$ ,  $(\text{C}_2\text{H}_5)_2\text{Cl}$ ,  $(\text{C}_2\text{H}_5)_2\text{Br}$ ,  $(\text{C}_2\text{H}_5)_2\text{I}$ .

<sup>2</sup> The molecules in question are  $\text{Hg}(\text{CH}_3)_2$ ,  $\text{Hg}(\text{C}_2\text{H}_5)_2$ ,  $\text{Zn}(\text{CH}_3)_2$ ,  $\text{B}(\text{CH}_3)_3$ ,  $\text{Sb}(\text{C}_2\text{H}_5)_3$ ,  $\text{Si}(\text{C}_2\text{H}_5)_4$ ,  $\text{Sn}(\text{C}_2\text{H}_5)_4$ ,  $\text{Pb}(\text{CH}_3)_4$ .

the supposed fact that the carbon atom is tetravalent in the molecule  $\text{CO}_2$ . But this formula assumes that there is direct action between the carbon and each oxygen atom, but not between the oxygen atoms themselves; this cannot be accepted as proved. Further, the formula appears to assume a double action of some kind between the carbon and oxygen atoms, such double action being represented by the double lines =.

59. Let us consider the meaning of these lines (—).

The carbon atom is tetravalent, i.e. the carbon atom combines with not more than four monovalent atoms: but the carbon atom has four equivalencies, or four valencies, or four bonds, or four units of affinity—each of these expressions is in common use—what does this mean<sup>1</sup>?

(1) It cannot mean that the force of affinity of a carbon atom is divided into four parts within that atom, for 'force' has no meaning apart from two or more reacting bodies: force is a name given by one of the parties to a transaction, but a transaction involves at least two transacting parties. The force between a carbon atom and another atom must vary with external conditions, probably with the distance, the mass, and the chemical nature (a vague term, but perhaps as good as can be given at present) of *both* atoms.

(2) The carbon atom has four equivalencies, or four units of affinity. This cannot mean that four parts of the carbon atom are chemically active, and the other parts inactive: such a hypothesis leads at present to contradictions (see appendix to Section 4); moreover in the present state of knowledge it is inadvisable to hazard hypotheses as to the inner structure of atoms in order to explain chemical phenomena. Atoms may not be homogeneous, but at present they are the ultimate particles to be considered in chemical changes.

(3) The expression under consideration cannot mean that the chemical energy of a carbon atom is divided, or is

<sup>1</sup> A paper of the greatest importance entitled 'Ueber die Vertheilung der Atome in der Molekel,' by W. Lossen, appeared in *Annalen*, 204. 265. I have made free use of this paper in the present chapter. (See also Claus, *Ber.* 14. 432; and Lossen, *ibid.* 760.)

always divisible into four parts. What is to be the unit of chemical work? the mass of matter fixed by a given atom? where then is the equivalency between one atom of oxygen with the mass 16 and two atoms of chlorine with the mass 71? Let a carbon atom combine with four hydrogen atoms, the total chemical energy of the atoms disappears; let a carbon atom combine with two atoms of oxygen, the total chemical energy of the atoms again disappears: but if the carbon atom possesses four 'units of affinity,' the oxygen atom two 'units of affinity,' and the hydrogen atom one 'unit of affinity,' the heats of formation of the two compound molecules ought to be equal. But the differences between the heats of formation of carbon compounds shew that the expression 'the carbon atom 'has four units of affinity' cannot mean that the chemical energy of the carbon atom is divisible into four parts, unless indeed the unit of affinity is variable, and is varied for each combination of carbon with other atoms<sup>1</sup>.

(4) The carbon atom has four equivalencies. Can this mean that the atom exerts force in four directions? A so-called 'valency' is then a direction. But there is no force exerted till the mutual atomic transaction begins; the carbon atom considered alone has therefore no 'valencies.' Take the molecule CO, force is exerted by the carbon on the oxygen atom; the remaining 'valencies' are sometimes said to be 'mutually satisfied,' i.e. on the present hypothesis, the carbon atom in the molecule CO exerts force in two directions on itself; but here again we have the hypothesis of the non-homogeneity of the carbon atom, and the existence of active and inactive parts in that atom.

(5) In the vibration of a carbon atom there are four points, at each of which mutual action can occur between this atom and another atom. On this supposition, a 'double link' would mean that mutual action occurs between the two atoms thus linked at two of these positions; e.g. the formula  $O=C=O$  means, that in performing a vibration the carbon atom acts twice on (and is twice acted on by) each oxygen

<sup>1</sup> For a view analogous to this see appendix to Section 4 of the present chapter, par. 98.



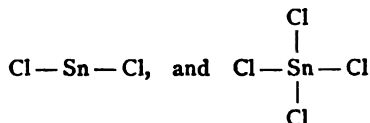
atom. But if so, surely a 'double link' would imply molecular stability, whereas it frequently means the reverse<sup>1</sup>.

The theory of units of affinity, or valencies<sup>2</sup>, or bonds, has been carried too far. It appears at first sight to give a dynamical explanation of the structure of molecules, but it has forgotten the two-sidedness of atomic transactions; it apparently affords a means of measuring atomic forces, but it has used a unit, undefined except as a quantity changeable at pleasure; it appears to simplify chemical formulæ, but it has really made them harder to understand by grafting on to the definite conception of atom the vague and unnecessary notion of 'bond.' When the molecule has been analysed and shewn to be an atomic structure, the theory of bonds has attempted to reconstruct the building, not by putting together the parts into which it had been separated, but by the use of new untried material called 'bonds,' the properties of which—if it has any—are unknown.

The theory of 'valencies' has gone too far because it has not gone far enough; it has not clearly distinguished the atoms of Dalton from the equivalents of Wollaston. In 1858 Kekulé recalled chemists to the consideration of elementary atoms as the fundamental units of which chemical compounds are built up; twenty-two years later Lossen has recalled the followers of Kekulé to the same all-important fact.

60. Let us turn back to the facts on which was based a classification of many elementary atoms into monovalent, divalent, tri, tetra, penta, and hexvalent groups (p. 121).

The atom of tin is divalent in the molecule  $\text{SnCl}_2$ : the atom of tin is tetravalent in the molecule  $\text{SnCl}_4$ : these statements are more shortly expressed by the graphic formulæ



<sup>1</sup> On the subject of 'double-bonds' see also appendix to Section 4 of this chapter.

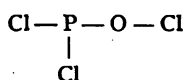
<sup>2</sup> It is important to distinguish between the expressions 'valency' and 'a valency.'

respectively ; a line (—) joining two atoms is used to denote direct action and reaction between these atoms.

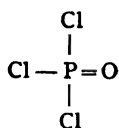
As thus interpreted, the statement, 'a given atom is mono-, di-, tri-, &c. valent in this or that molecule,' has a definite and defined meaning.

Lossen (*loc. cit.*) insists on the necessity of naming the molecule in which a given atom occurs, when the valency of that atom is stated. Such a general statement as 'the atom of carbon is tetravalent' must be taken as meaning 'one atom of carbon, so far as we know at present, is never directly combined with more than four other atoms,' or 'four is the maximum number of atoms which can come within the "binding-sphere" of a carbon atom in any molecule' (Lossen). The special statements, 'in the molecule of carbon dioxide the carbon atom is divalent,' 'in the molecule of carbon monoxide the carbon atom is monovalent,' mean, that in one molecule the carbon atom acts directly on—and is acted on by—two other atoms, and in the other molecule on one other atom ; or, in the first molecule there are two atoms, and in the second molecule one atom, within the binding-sphere of the carbon atom.

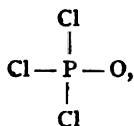
As illustrations of this—Lossen's—way of regarding valency, let us take the molecule  $\text{POCl}_3$ . 'In this molecule the phosphorus atom is trivalent : ' the formula



expresses this statement completely ; there is direct action, and reaction, between the phosphorus atom and three other atoms, and as the chlorine atom is always monovalent, one of the three atoms must be oxygen. But it is sometimes said, 'in phosphoryl chloride the phosphorus atom is pentavalent,' and the formula



is used as expressing this statement. But this is equivalent to saying, the phosphorus atom has five 'bonds,' three of which are 'satisfied' by chlorine atoms, and two by an oxygen atom. The objections to such a statement have been already considered. Assuming that there is direct action, and reaction, between the phosphorus atom and each of the other atoms comprising the molecule  $\text{POCl}_3$ , Lossen's formula would express the structure of this molecule thus



This formula would be translated into the corresponding system of nomenclature by saying, 'in this molecule the 'phosphorus atom is tetravalent.'

Again, the formulæ of carbon monoxide and dioxide are generally written  $\text{C}=\text{O}$  and  $\text{O}=\text{C}=\text{O}$  respectively, and the carbon atom is said to be tetravalent in both, i.e. in each the carbon atom has four 'bonds,' in  $\text{CO}$  two are satisfied by oxygen and two satisfy one another, in  $\text{CO}_2$  on the other hand each oxygen atom satisfies a pair of bonds. Lossen would write the formulæ of these molecules as  $\text{C}-\text{O}$  and  $\text{O}-\text{C}-\text{O}$ , and say, the carbon atom is monovalent (i.e. acts directly on a single atom) in the first, and divalent (i.e. acts directly on two atoms) in the second<sup>1</sup>. The first pair of formulæ almost necessarily implies that the force between the carbon and the oxygen atoms in  $\text{CO}$  is equal to that between the carbon and each oxygen atom in  $\text{CO}_2$ , and this dynamical conception is strengthened by the use of such expressions as the 'bonds are satisfied,' &c. No such assumption is made by Lossen's formulæ. Most probably the force between any pair of atoms varies in different molecules in which this pair of atoms is present; whether this is so or not, and if it is so, whether the force is greater in molecule  $a$  than

<sup>1</sup> Of course  $\text{CO}_2$  may be written  $\text{O}-\text{C}-\text{O}$ ; whether there is or is not *direct* action between the oxygen atoms must be determined by a general study of the chemical habitude of the molecule.

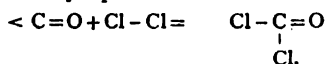
in molecule *b* (or *vice versa*), is a dynamical question which cannot be solved, at present, by the theory of valency; it is a question outside of this theory; and it is surely better to recognise this, and, especially in view of the masses of new facts and new hypotheses which are showered on chemists, to make the theory of valency definite, even if this be done by narrowing its scope.

61. But it is said, CO is an unsaturated, CO<sub>2</sub> a saturated molecule. What then it may be asked is a saturated molecule? A saturated molecule, it is usually answered, is one which exhibits no tendency to combine directly with other molecules, or atoms; an unsaturated molecule on the other hand is ready to form additive compounds. Now the molecule CO readily combines with Cl<sub>2</sub> to form the new molecule COCl<sub>2</sub><sup>1</sup>, therefore CO is an unsaturated molecule: to this it may be answered, with Lossen, that as Cl<sub>2</sub> readily combines with CO, Cl<sub>2</sub> is an unsaturated molecule. Definitions so indefinite as 'readiness or unreadiness to form additive compounds' do not help us to understand the apparently precise formulæ, e.g. <C=O and O=C=O, in which these definitions are expressed. The expressions 'unsaturated molecule' and 'molecule with free bonds' are frequently used as synonymous; if we can attach a precise meaning to the latter expression we shall have gained the definition we are seeking. The molecule C<sub>2</sub>H<sub>4</sub> very easily combines with bromine to form C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>, that is to say, C<sub>2</sub>H<sub>4</sub> acts as an unsaturated molecule, and therefore contains 'free bonds'; but the generally adopted

formula,  $\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array}$ , represents the two carbon atoms as joined

by a double bond; we should expect this molecule to be very unready to form an additive compound. Moreover molecules supposed to contain 'free bonds' are sometimes very easily produced from others containing only 'satisfied bonds'; e.g. NO is formed by the action of water on

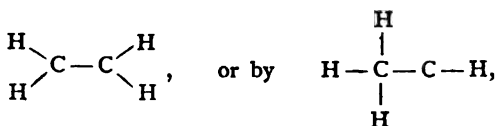
<sup>1</sup> This reaction is usually represented thus:



$N_2O_3$  or  $N_2O_4$  [ $-N=O$ , from  $O=N-O-N=O$  or  $O=N-O-O-N=O$ ]: this reaction appears to be opposed to all ideas, however vague, which can be associated with the phrase 'free bonds.' But some chemists say that 'a double bond' is the same thing as 'two free bonds': very probably they are right; one does not venture much in asserting identity between two undefined and undefinable propositions.

We appear then to gain nothing by saying that an unsaturated molecule is one containing free bonds, unless indeed knowledge is advanced by explaining the unknown in terms of the unknowable<sup>1</sup>.

62. Lossen attempts to attach precise meanings to the expressions 'saturated' and 'unsaturated' molecules. A saturated molecule, he defines to be, one in which each polyvalent atom directly acts on, and is acted on by, its maximum number of monovalent atoms (see formula, p. 139, par. 70). An unsaturated molecule, he defines to be, a molecule in which one, or more, polyvalent atom acts directly on, and is acted on by, less than its maximum number of monovalent atoms. Saturated molecules, as thus defined, can combine only with polyvalent atoms, such combination being preceded by rearrangement of the mutual direct atomic actions: unsaturated molecules are able to combine directly with monovalent atoms. As an example of an *unsaturated molecule*, we may take the compound  $C_2H_4$ . Granting that the carbon atom is tetravalent, it follows that the molecule  $C_2H_4$  is unsaturated, because, whether we suppose the mutual atomic actions to be represented by the formula

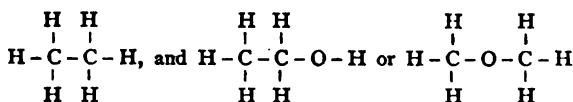


<sup>1</sup> Lossen points out that molecules described as 'containing free bonds' can usually take part in reactions wherein condensation of volume occurs, e.g.  $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ ,  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ ,  $2\text{NO} + \text{O}_2 = \text{N}_2\text{O}_4$  (or at higher temperatures  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ ),  $4\text{NO} + \text{O}_2 = 2\text{N}_2\text{O}_3$ , &c. [See also appendix to Section 4 of this chapter.]

at least one carbon atom is directly combined with less than its maximum number of monovalent atoms.  $C_2H_4$  can combine with monovalent atoms, e.g. it forms  $C_2H_4Br_2$ . The compound  $C_2H_6$  affords an example of a *saturated molecule*. As the valency of the carbon atom is four,  $C_2H_6$  is necessarily saturated, because, however the interatomic actions are represented in a formula, each carbon atom must be regarded as combined with its maximum number of monovalent atoms. The molecule  $C_2H_6O$  can be produced from  $C_2H_6$ , but the reactions which occur in this change, and also the properties of  $C_2H_6O$ , shew that the interatomic actions are differently arranged in the two molecules  $C_2H_6$  and  $C_2H_6O$ <sup>1</sup>.

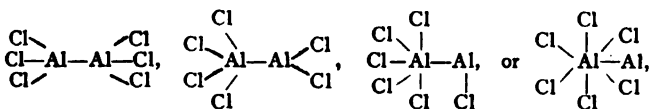
63. It is evident that the valency of only a minority of the elementary atoms can be considered as fairly well established. In order to determine the valency of an elementary atom we ought to have several gasifiable compounds of that element with elements whose atoms are monovalent, the molecules of such compounds containing not more than one atom of the given element<sup>2</sup>. When we know of but one such compound we are unable to fix the valency; we may however say that the valency of the atom is probably an odd or an even number according as its valency in the given

<sup>1</sup> The possible formulæ are,—



respectively.

<sup>2</sup> Thus the valency of Al cannot be determined from the molecule  $Al_2Cl_6$ . The formula  $Al_2Cl_6$  might be written



the valency of the aluminium atom varying from 1 to 7. The first of these is most probably correct, considering the general properties of the molecule  $Al_2Cl_6$ , but the evidence is not sufficient to decide that Al belongs to the group of tetra-valent atoms.

molecule is an odd or even number<sup>1</sup>; and we may also conclude that the number which expresses the valency of the given atom in the special molecule under consideration will also express its valency in many other molecules. Although the valency of an atom has been determined from a consideration of several molecules containing that atom, it is still possible that this number does not express the true valency; but until the number is proved to be too small it must be used as the true valency in all questions regarding structural formulæ of molecules containing the given atom<sup>2</sup>.

When no molecule containing monovalent atoms, combined with a single atom—or even with more than one atom—of a given element can be obtained, any number assigned as the valency of the atom of that element must be very doubtful.

Many non-gasifiable compounds containing monovalent atoms combined with atoms of a single other element are known (e.g. many metallic haloid compounds): if the molecular weights deduced for these compounds by the aid of considerations such as those sketched on pp. 74—77 are assumed to be the true relative weights of the molecules of these solid compounds, and if those generalisations which have been made concerning the arrangement of atoms in gaseous molecules are assumed to hold good for the molecules of solids also, then the valency of many elementary atoms not included in the table on p. 121 could be determined. Thus, if we assume that the general formula  $MX$  represents the atomic structure of the molecules of the solid haloid salts of the alkali metals ( $M = K, Na, Li, \&c.$  and  $X = F, Cl, Br, \text{ or } I$ ) then the atoms of these metals are most probably monovalent. Most of the generally accepted formulæ for salts of alkali metals may be written with the atoms of these metals represented as each in direct com-

<sup>1</sup> When 'valency of an atom' is spoken of without mention of the valency in a particular molecule, the expression is always to be understood as defined on p. 122, see also p. 127.

<sup>2</sup> If this rule is not attended to endless confusion arises, and the whole theory of valency becomes merely an amusing exercise of fancy.

bination with only one other atom, but whenever this arrangement has become somewhat unsatisfactory chemists have not hesitated to assume that the atoms of the alkali metals may be tri- penta- or even heptavalent, i.e. may each act on, and be acted on by, 3, 5, or 7 other atoms. So with other elements; from a consideration of solid or liquid compounds only no trustworthy conclusions as to the valencies of the atoms in the molecules of these compounds can be deduced. It is so easy, after making the two fundamental assumptions stated above, to make an indefinite number of further assumptions; it becomes so pleasant to manipulate formulæ on paper, that it is certainly better—in the present state of knowledge—to apply the theory of valency only to gaseous molecules. It is very probable that the valency of the elementary atoms varies periodically with variations in the relative weights of these atoms: if this general statement is thoroughly established, the exact nature of the periodic function is determined, and the true atomic weights of all the elements are fixed, we shall have in the *Periodic Law* a most important method for determining valencies. But a great deal of work must be done before this 'law' can be applied otherwise than generally and tentatively to questions of valency (see chap. III. par. 115).

#### SECTION IV. *Allotropy and Isomerism.*

64. Having gained the conception of a molecule as composed of atoms, each directly acting on, and being acted on by, a definite number of other atoms, we at once regard the molecule as a structure; we recognise what Frankland in 1852 happily called 'limited molecular mobility.' A structure involves arrangement of parts, subordination of less to more important parts; it supposes the existence of definite actions for fulfilling which the structure is adapted; in a word, structure means correlation of properties and material configuration<sup>1</sup>.

<sup>1</sup> When 'arrangement of atoms in the molecule' is spoken of, or when a similar phrase is used, it is to be taken as implying only a rough approximation



And when we consider the properties of individual molecules the justness of thus regarding each as a definite atomic structure becomes more apparent. We find many compound molecules containing the same number of the same elementary atoms yet exhibiting markedly different chemical and physical properties, i.e. we find the phenomenon of *Isomerism*: how can we account for this except by assuming (1) that each molecule has a definite atomic structure, and (2) that the same atoms may be differently arranged in different molecules?

65. A knowledge of the atomic configurations of series of molecules, supposing this to be gained, must be supplemented by a knowledge of the way in which the energy of each molecule varies with variations in the configuration and motion of its constituent atoms, before a complete knowledge of the dynamical properties of these molecules is possible. But chemistry is yet far from this goal; she is obliged to be content with a very partial and sometimes very vague knowledge concerning the relative atomic configurations of a few molecules; she has hardly entered on the second part of her task.

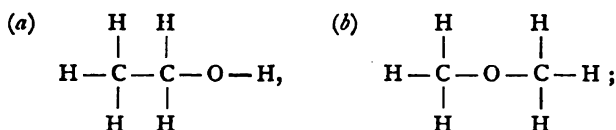
66. Granting then that variations in the properties (chemical and physical) of molecules accompany variations in the atomic configurations of these molecules, it is conceivable that the latter variations may consist of

- (1) variations in the relative positions of the atoms,
- (2) variations in the distances between the atoms, their relative positions being constant.

To illustrate this point, let us take the molecule  $C_2H_6O$ . More than one compound exists the molecules of which have the atomic composition expressed by this formula. On the first assumption, viz. that variation of properties is to be correlated with variations in the relative positions of the

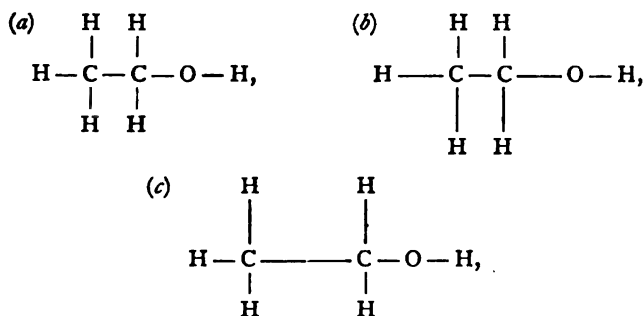
to a knowledge of atomic arrangements. Structural formulæ sum up facts of formation and decomposition, and, assuming the fundamental positions of the molecular theory, exhibit, in a rough and general way, connections between these facts and the directions of the mutual actions of the atoms in the molecules of the compounds formulated. No attempt is made in these formulæ to express quantitative measurements of atomic interactions.

atoms in the molecule, we find that there are two possible arrangements of the two carbon, six hydrogen, and one oxygen atoms (assuming the valency of the carbon, hydrogen, and oxygen atom to be 4, 1, and 2 respectively), viz.



hence, two compounds, each having the composition expressed by the empirical formula  $\text{C}_2\text{H}_6\text{O}$ , may exist.

But if we make the second assumption, viz. that variation of properties is to be correlated with variations in the distances between the atoms in the molecule, the relative positions of these atoms remaining unchanged, we may have an apparently unlimited number of compounds of the formula  $\text{C}_2\text{H}_6\text{O}$ ; such compounds might perhaps be represented in this way,—



and so on.

Now as only two compounds,  $\text{C}_2\text{H}_6\text{O}$ , are known to exist, we have a presumption in favour of the first supposition: much stress cannot however be laid on this argument. Moreover if the second of the two suppositions is correct, then any molecule containing two atoms should be capable of existing in more than one modification; in other words, every diatomic molecule should be capable of shewing isomerism. But there is no certainly-established instance of isomerism exhibited by any molecule containing less than three atoms;

therefore, as the assumption that variations of properties exhibited by compounds having the same composition and same molecular weight are connected with variations in the relative positions of the atoms composing the molecules of these compounds, suffices to explain the vast majority of well-authenticated cases of isomerism among gaseous molecules, we conclude that it is better, at any rate at present, to build the general theory of isomerism on this hypothesis<sup>1</sup>.

67. But before more fully considering this subject, it will be well to glance at the allied phenomena of *allotropy* and *polymerism*.

The table on p. 42 shews that of the thirteen elements whose molecular weights have been determined by the help of Avogadro's law, four, viz. oxygen, sulphur, selenion and iodine (probably bromine also) possess a smaller molecular weight at high than at lower temperatures;—the number of atoms in the molecule of oxygen at temperatures below about 300°, and under special conditions is 3, at temperatures above 300° it is 2; the molecule of sulphur at temperatures not much higher than the boiling point of that element contains 6 atoms, and at somewhat higher temperatures 2 atoms; the number of atoms in the molecule of selenion varies from 3 to 2, and in the molecule of iodine (and probably also in that of bromine) from 2 to 1, according to temperature. We know that the properties correlated with the existence of the triatomic molecule  $O_3$  differ much from those which characterise the diatomic molecule  $O_2$ : no experiments have been made to compare the properties of the hexatomic with those of the diatomic molecules of sulphur, of the triatomic with the diatomic molecules of selenion, and of the diatomic with the monatomic molecules of iodine.

Of the 15 or 16 nonmetallic elements, phosphorus and

<sup>1</sup> The supposition that isomerism may be due to variations in the distances between atoms, the relative positions of which remain unchanged, appears to be opposed to the results of physical experiments which are in agreement with deductions made from the kinetic theory of gases. See Lossen, *loc. cit.* p. 269.

arsenic, boron, carbon and silicon—besides sulphur and selenium—exhibit marked variations in physical and chemical properties when in the solid state. We certainly are not justified in unconditionally asserting that these variations of properties accompany differences in the atomic configurations of the molecules, or differences in the numbers of atoms in the molecules, of red and yellow phosphorus, or of octahedral and prismatic sulphur, &c. When the differences in properties are chiefly physical (e.g. differences in crystalline form, in specific gravity, in melting points, &c.), they may very probably be correlated with differences in the molecular, rather than in the atomic, configurations of the various modifications of the element in question<sup>1</sup>.

Be this however as it may, the differences experimentally shewn to exist between the properties of the molecules of gaseous oxygen and ozone are explicable in terms of the molecular theory only by admitting that the properties of a molecule are dependent not only on the nature but also on the number of the atoms which compose it<sup>2</sup>.

The marked chemical differences between red and yellow phosphorus would lead us to expect that the molecular weight of gaseous phosphorus would be found to vary with variations of temperature: such variations have not however as yet been observed<sup>3</sup>.

<sup>1</sup> See section 5. of present chapter.

<sup>2</sup> It ought to be noted that change from one allotropic form to another is accompanied by evolution or absorption of heat; see *post*, chap. IV., par. 125.

<sup>3</sup> V. Meyer states [*Ber.* 14. 1455; see also *do.* 13. 1116 note] that the vapour densities of phosphorus and arsenic at very high temperatures point to the existence of molecules weighing less than  $P_4$  and  $As_4$  respectively.

There are some interesting observations bearing on the subject of allotropy by W. Spring in the *Berichte* [see especially 16. 1002—3]. Spring finds that when an element which exhibits allotropy is subjected to great pressure, that modification which has the greatest specific gravity is produced. Yellow phosphorus is changed into red by compression: red phosphorus and sulphur do not combine until heated to  $260^\circ$ , i.e. to the temperature at which red is changed to yellow phosphorus; red phosphorus does not combine with sulphur when the two are subjected to a pressure of 6500 atmospheres, at which pressure many metallic sulphides are produced. Hence Spring concludes that red phosphorus is less chemically energetic than yellow; and generally that the more a solid substance is rendered dense, the

68. The names *allotropy* and *polymerism* are applied to analogous phenomena exhibited by elements and compounds respectively.

If two molecules exist, consisting of the same elementary atoms, but one heavier than the other, the heavier molecule is said to be a 'polymeric modification,' or a 'polymeride' of the other:—thus  $C_{10}H_{20}$  is a polymeride of  $C_5H_{10}$ ,  $C_{12}H_{24}$  is a polymeride of  $C_6H_{12}$ ,  $H_3C_3N_3O_3$  is a polymeride of  $HCNO$ ,  $C_6H_{12}O_3$  is a polymeride of  $C_2H_4O$ . Glucose,  $\alpha C_6H_{12}O_6$ , is not however regarded as a polymeride of ethylene oxide,  $C_2H_4O$ : the name is restricted to those molecules whose weight is a multiple of that of other molecules, and which are obtained by simple reactions, generally by the action of heat, from these other molecules. Thus, ethaldehyde,  $C_2H_4O$ , is easily polymerised, e.g. by the action of a very little hydrochloric or sulphuric acid, with formation of paretaldehyde,  $C_6H_{12}O_3$ ; but the latter body is not directly obtainable from ethylene oxide, although the molecule of this compound, like that of ethaldehyde, contains 2 atoms of carbon, 4 of hydrogen, and 1 of oxygen.

But few examples of undoubted polymerism are furnished by compounds of the elements other than carbon; one of the most marked cases is the molecule  $N_2O_4$ , which is a polymeride of  $NO_2$ , another is furnished by the molecules  $Sn_2Cl_4$  and  $SnCl_2$ .

69. The phenomena summarised in the term *isomerism*, i.e. the existence of molecules characterised by different properties but containing the same number of the same atoms, must now be examined in some detail.

Isomeric compounds are generally said to be '*metameric*' when they belong to different chemical types. This statement does not of course furnish a definition of metameric compounds; but it is sufficient. Various hydrocarbons, all possessed of the general properties of paraffins, but each differing in some properties—chemical and physical—from the others, are represented by the formula  $C_nH_{2n+2}$ : various hydro- more is its chemical activity decreased. Red phosphorus he regards as a *polymeride* of yellow phosphorus.

carbons, all benzenes, but each characterised by its own special properties, are represented by the formula  $C_8H_{10}$ : the different paraffins— $C_8H_{16}$ , or the different benzenes,  $C_8H_{10}$ —are said to be *isomerides* one of the other. But although two molecules are represented by the formula  $C_2H_6O$ , yet these belong to very different types, or groups of compounds; one is a primary alcohol, the other an ether: so again allylic alcohol and dimethyl ketone have both the formula  $C_3H_6O$ , but these bodies are altogether distinct in their chemical properties—such compounds are said to be metameric. *Metamerides* are thus seen to be a sub-class included in the larger class of isomeric compounds.

A few inorganic compounds exhibit phenomena which may be explained by supposing the existence of isomeric molecules, but it is only when we study the compounds of carbon that we are obliged to admit that molecules may contain the same numbers of the same atoms but differ in chemical and physical properties.

70. The theory of valency having led to the recognition of the molecule as a structure, may be carried further; it may guide us in determining the probable relative structures of isomeric molecules (see note to p. 133).

If it be granted that isomerism is correlated with different relative positions of atoms, but not with different distances between atoms in the same relative positions in the molecule<sup>1</sup>, (see p. 134), it follows, that, a molecule containing not more than two atoms cannot exhibit isomerism. The maximum number of monovalent atoms which can be combined with polyvalent atoms in a molecule is found by the formula<sup>2</sup>

$$n_1 = n_3 + 2n_4 + 3n_5 + 4n_6 + 2,$$

where  $n_1$ ,  $n_3$ ,  $n_4$ , &c. represent the numbers of monovalent, trivalent, tetravalent, &c. atoms in the molecule. Any molecule in which the value of  $n_1$  agrees with that deduced from

<sup>1</sup> Such formulæ as  $O=N-$  and  $=N-O-$  are really, at present, the same.

<sup>2</sup> See Lothar Meyer, *Die Modernen Theorien der Chemie* (4th Ed.), pp. 218 *et seq.*, of which pages free use has been made in these paragraphs.

this formula must necessarily be a saturated molecule<sup>1</sup>. But each polyvalent atom in a molecule does not necessarily act on the maximum number of other atoms; in many molecules

$$n_1 < n_3 + 2n_4 + 3n_5 + 4n_6 + 2 :$$

when this holds good, some polyvalent atoms must have within their 'binding spheres' less than the maximum number of atoms, in other words, some atoms usually divalent must, *in this molecule*, be monovalent, or some usually trivalent must, *in this molecule*, be divalent &c. This is expressed in ordinary nomenclature by saying that some of the polyvalent atoms must be linked by 'double' or 'treble bonds', or that some of the 'bonds' (sometimes it is said, of the 'affinities') of the polyvalent atoms must be 'mutually satisfied.' But I have tried to shew that these expressions are delusive, and that Lossen's method of regarding valency is preferable to any yet proposed.

71. The number of ways in which the atoms comprising a complex molecule may be arranged is evidently very great<sup>2</sup>: to determine the maximum number of possible isomerides of a given formula is a purely mathematical problem. At present we seem justified in concluding that many atomic configurations which are mathematically possible, are physically impossible; this is equivalent to saying that the stability of molecules does not depend solely on the valencies of their constituent atoms. To determine which of the possible configurations of a given number of atoms are stable; to generalise the connections undoubtedly existing between molecular structure and stability, and also between this structure and the functions of the molecule or of parts thereof; this is the task that chemists are now elaborating.

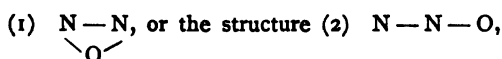
<sup>1</sup> See definition on p. 130.

<sup>2</sup> Thus, Prof. Cayley, *Brit. Ass. Reports* for 1875, p. 257, gives the following statement, exhibiting the relations between the number of carbon atoms in the molecules of paraffins and the number of isomeric modifications of each molecule allowed by the theory of valency.

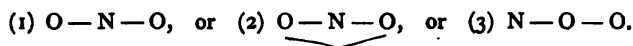
Number of carbon atoms in molecule of paraffin,	1.	4.	7.	10.	12.	13.
Number of possible isomerides	...	...	1.	2.	9.	75. 357. 799.

72. The molecular formula of a compound alone sometimes gives us a considerable amount of information regarding the structure of the molecule of that compound. Thus we appear justified, at present, in making the following assertions; (1) molecules containing only monovalent atoms cannot exhibit isomerism; (2) molecules containing a single polyvalent atom united with monovalent atoms only cannot exhibit isomerism; (3) isomerism cannot be exhibited by molecules containing two polyvalent atoms united with monovalent atoms, provided the latter are all atoms of the same element, or all but one atoms of the same element, when the two polyvalent atoms are themselves atoms of the same element.

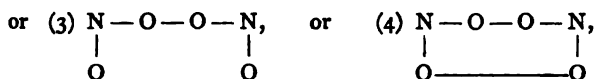
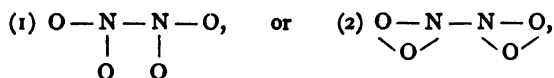
73. Any molecule containing more than two atoms and not belonging to one of the classes above defined, may exhibit isomerism. The possible variations of structure even in molecules containing a small number of atoms may be large. Thus  $N_2O$  may have the structure



(neither the nitrogen nor the oxygen atoms can act on *more* than two atoms, i.e. neither can be more than divalent<sup>1</sup>).  $NO$  can be regarded only as  $N-O$ .  $NO_2$  may be



$N_2O_4$  may have many structures, e.g.



or (5)  $N-O-O-O-O-N$ , or (6)  $N-N-O-O-O-O$ , &c.

In the case of  $N_2O$ , the first of the possible structures

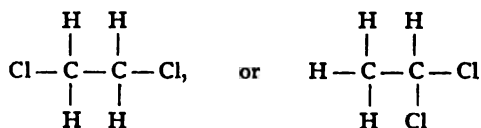
<sup>1</sup> Lossen's nomenclature and notation are used here and generally throughout the rest of this book.



better represents the arrangement of atoms in this molecule than the other, inasmuch as the reactions of this compound shew that there is no difference in the functions of the two nitrogen atoms in the molecule; for a similar reason the third formula for  $\text{NO}_2$  and the sixth for  $\text{N}_2\text{O}_4$  are inadmissible; the fifth formula for  $\text{N}_2\text{O}_4$  is improbable because, among other reasons, it would lead to  $\text{N}-\text{O}-\text{O}$  as the formula for  $\text{NO}_2$ ; the fourth formula for  $\text{N}_2\text{O}_4$  would lead us to expect that this compound when heated would decompose into  $\text{NO}$  and  $\text{O}_2$ , but we know that it gives  $2\text{NO}_2$ . Formulæ (1) and (2) very simply express the formation of  $\text{N}_2\text{O}_4$  by cooling  $2\text{NO}_2$ , and the formation of  $2\text{NO}_2$  by heating  $\text{N}_2\text{O}_4$ , and therefore the structure of the molecule  $\text{N}_2\text{O}_4$  is more probably expressed by one or other of these formulæ than by any other of the six given above.

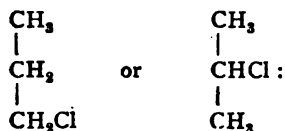
The compounds of carbon present the best field for the study of isomerism.

It has been already stated that a molecule containing two carbon (tetravalent) atoms united with five monovalent atoms of one element and one monovalent atom of another element, (i.e. a molecule of the form  $\text{C}_2\text{X}_5\text{X}'$ ) cannot exhibit isomerism. If however there are four monad atoms of one kind, and two of another in the molecule (if the form of the molecule is represented by the symbol  $\text{C}_2\text{X}_4\text{X}'_2$ ) isomerism becomes possible; thus  $\text{C}_2\text{H}_4\text{Cl}_2$  may have the structure

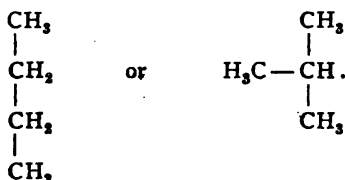


(or more shortly,  $\text{CH}_2\text{Cl}$  and  $\text{CH}_2\text{Cl}$  ) . But when three carbon

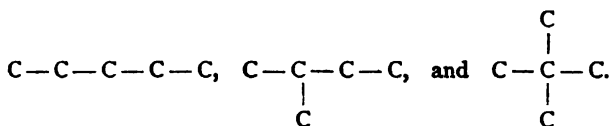
atoms combine with monovalent atoms, the existence in the molecule thus produced of a single monad atom of an element different from that forming the other monad atoms renders isomerism possible; thus  $\text{C}_3\text{H}_7\text{Cl}$  (which belongs to the general form  $\text{C}_3\text{X}_7\text{X}'$ ) may have the structure



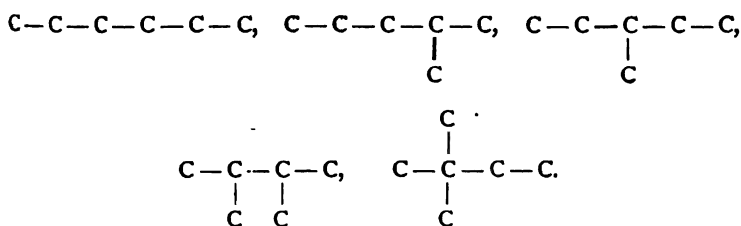
So also four molecules  $\text{C}_3\text{H}_5\text{Cl}_2$ , five molecules  $\text{C}_3\text{H}_5\text{Cl}_3$ , six  $\text{C}_3\text{H}_4\text{Cl}_4$ <sup>1</sup>, five  $\text{C}_3\text{H}_3\text{Cl}_5$ , &c. may exist. Molecules containing four, or more than four atoms of carbon combined with monovalent atoms may exhibit isomerism even when all the monad atoms are of one kind, (i.e. molecules of the general form  $\text{C}_4\text{X}_{10}$ ): thus  $\text{C}_4\text{H}_{10}$  may have the structure



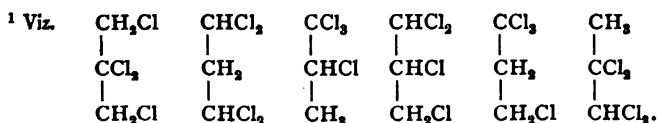
Molecules containing five carbon atoms may have these atoms arranged in three ways, as represented by the formulæ



When six carbon atoms are present in the molecule these atoms may be arranged in five ways, viz.



When eight carbon atoms are present, they may be arranged

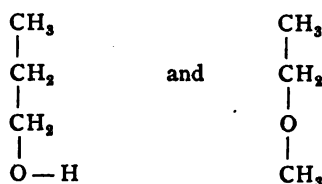


in 18 different ways, &c. The maximum number of monovalent atoms which can be combined with any of these arrangements of carbon atoms is found by the formula  $n_1 = 2n_4 + 2$  where  $n_4$  = number of carbon atoms<sup>1</sup>. But all the carbon atoms in a molecule are not necessarily tetravalent in that molecule (in the ordinary nomenclature some of the carbon atoms may be doubly or trebly linked to one another, or there may exist 'free affinities'). Now the general formula given on p. 139, viz.

$$n_1 = n_3 + 2n_4 + 2$$

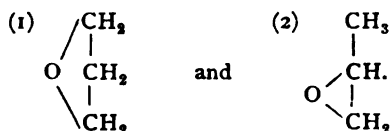
shews that the maximum number of monad atoms in such a molecule is dependent only on the number of trivalent and tetravalent, and is independent of the number of divalent, carbon atoms in the molecule. But in applying this formula it is assumed that the number of carbon atoms which are actually trivalent, and of those which are actually tetravalent in any given molecule, can be determined. It is better to represent the molecule of a carbon compound, if possible, as containing only tetravalent carbon atoms: in many cases however this cannot be done; in any case the reactions of the compound must be studied before a formula is given to it.

Let us suppose we are required to assign formulæ to compound molecules containing carbon, hydrogen, and oxygen atoms. When the equation  $n_1 = 2n_4 + 2$  is satisfied, the structural formula assigned to the molecule must evidently contain only tetravalent carbon atoms; several such formulæ may however be possible,—thus for the molecule  $C_3H_8O$ , two structural formulæ

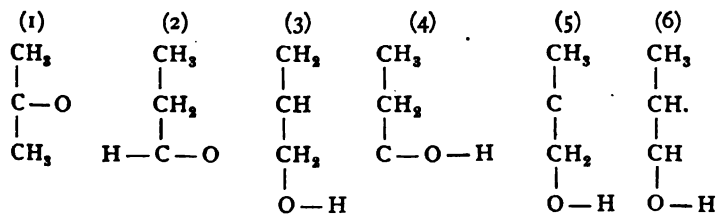


<sup>1</sup> See Lothar Meyer, *loc. cit.* pp. 240—242.

fulfil the conditions required. In accordance with generalisations which have been made correlating structure and properties, the first of these formulæ belongs to a primary alcohol, the second to a mixed ether: two, and only two compounds,  $C_3H_8O$ , are known, one exhibiting the properties of a primary alcohol, the other those of a mixed ether. When however  $n_1 < 2n_4 + 2$ , and divalent atoms are also present in the molecule, the formula may contain only tetravalent carbon atoms, or it may contain tetravalent, and also di- or trivalent carbon atoms. Thus in  $C_3H_8O$   $n_1 = 2n_4$ ; two structural formulæ are possible wherein each carbon atom is tetravalent, viz.



Each of these is the formula of an ether; in propylene oxide we have an ether the properties of which shew that it is probably described by the first of these formulæ. Six structural formulæ are possible for the molecule  $C_3H_8O$ , provided some of the carbon atoms may be tri- or divalent. Three compounds having this formula (besides propylene oxide) are known; of these, one is a ketone, i.e. belongs to a class of compounds the molecules of which are generally regarded as containing a carbon and an oxygen atom in direct union; another is an aldehyde, i.e. belongs to a class of compounds the molecules of which are regarded as containing a carbon atom in direct combination with one oxygen and one hydrogen atom; and the third is an alcohol, probably a primary alcohol. The six possible formulæ are



The first and second formulæ contain each one trivalent carbon atom, and the oxygen atom is monovalent in both, the third contains one trivalent, the fourth and fifth each one divalent carbon atom, and the sixth contains two trivalent carbon atoms. Formulæ (1) and (2) are appropriated by dimethyl ketone and propaldehyde respectively; of the remaining four, (3) and (5) represent allylic alcohol as a primary, (6) as a secondary, and (4) as a tertiary alcohol. Judging from the general reactions of allylic alcohol, this compound is probably a primary alcohol. Formula (3) is preferable to (5), because the latter would lead us to expect acetic acid  $\begin{pmatrix} \text{CH}_3 \\ | \\ \text{CO}_2\text{H} \end{pmatrix}$  as one of the

products of oxidation of allylic alcohol; inasmuch as acetic acid is not produced in this oxidation, formula (3) more probably expresses the structure of the molecule of allylic alcohol than any other possible formula.

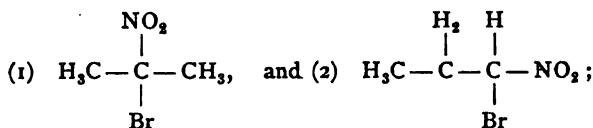
74. In these examples of the method adopted for determining the structural formula of a compound, several generalisations concerning the connection of structure with properties have been assumed: e.g. that, if a given compound exhibits aldehydic properties, the structural formula of the molecule is to be written as containing the atomic group COH; that two structures are possible for this group, one in which the carbon atom acts directly on the oxygen and on the hydrogen atoms (H—C—O), the other in which direct action occurs only between the carbon and the oxygen atoms (C—O—H); further, the first of these structures is assumed to be correlated with the group of properties connoted by the word 'aldehydic,' the second with the properties connoted by the expression 'tertiary alcoholic.' When therefore a new carbon compound is discovered, it is necessary to determine, as far as possible, to what group of compounds it belongs; the existence of a certain atomic group (or groups) in the molecule of the compound may then generally be predicated, and the number of possible structural formulæ may thus be considerably diminished. But the classification of the carbon compounds is certainly not yet complete;

hence arise two difficulties, (1) a new compound may belong to a class no other member of which has been previously examined, in which case no class-group can be assigned to the formula of the new compound; or (2) a compound may be prepared whose properties indicate that it belongs to one of the known classes, and yet the group which generally marks this class may not be present in the molecule of this particular compound. The following cases may be taken as illustrations of these difficulties.

(1) It was known that the action of nitrous acid on carbon compounds containing the group  $\text{NH}_2$  (amido-derivatives) resulted in the production of compounds differing from the original by containing  $\text{OH}$  in place of  $\text{NH}_2$ ; but when nitrous acid acted on certain amido-derivatives of benzene, compound molecules containing one nitrogen atom more and two hydrogen atoms less than the original molecule were obtained. The reaction appeared to be abnormal. Several of the new compounds were prepared, their properties were studied, and the existence of a new class of carbon compounds was recognised, the relations of which to other classes appeared to be best summarised in formulæ containing the characteristic group  $-\text{N}_2-$ .

Certain peculiar and definite properties appear to be always associated with this group; it has recently been shewn that the formation of molecules containing this group and derived from compounds of the 'fatty' or 'paraffinoid' series is possible under special conditions.

(2) As the result of long and varied experience, the generalisation has been made that the molecules of carbon acids contain the characteristic group  $\text{H}-\text{O}-\text{C}-\text{O}$ , but from time to time compounds have been prepared exhibiting acid properties, but possessed of a molecular structure from which the characteristic group is absent. Thus  $\text{C}_3\text{H}_8$  yields  $\text{C}_3\text{H}_7\text{NO}_2$ , and from this compound two isomerides  $\text{C}_3\text{H}_7\text{BrNO}_2$  are obtained, one of which is a monobasic acid, while the other does not shew acid properties; the possible formulæ for these isomerides are



from a consideration of the general properties of the two isomerides and their relations to other compounds, the second formula is assigned to the acid. Hence we are obliged to conclude that although most known carbon acids are characterised by the atomic group  $\text{H}-\text{O}-\text{C}-\text{O}$ , yet a substance may be a true acid in the molecule of which this group is not present.

A very instructive example of the difficulties to be overcome before a general structural formula can be assigned to a group of carbon compounds, is afforded by the investigations which have been, and are being made into the constitution of the quinones<sup>1</sup>.

These examples (and others might easily be added) shew how undesirable it is to regard the present system of classification of carbon compounds as final. As facts are accumulated, the atomic grouping which was regarded as a class-group sometimes becomes the group of a larger class, sub-classes being formed, each characterised by its special group, and yet each containing the class-group. Thus, from the analogy between metallic hydroxides and alcohols, and for other reasons, the group  $\text{O}-\text{H}$  was assigned to alcohols (e.g.  $\text{C}_2\text{H}_5.\text{OH}$ ,  $\text{C}_2\text{H}_7.\text{OH}$ , &c., &c.); but it became evident that a sub-division of this great group was required; facts were amassed and formulæ devised to generalise these facts, until most chemists are now agreed that the molecules of those alcohols called 'primary' (which yield certain definite products when oxidised, &c.) contain the atomic group  $\text{H}-\text{O}-\text{CH}_2$ , the molecules of those called 'secondary' (and which yield other, but also definite products when oxidised) contain the group  $\text{H}-\text{O}-\text{C}-\text{H}$ , and the molecules of those called 'tertiary' (which yield a third distinct set of products when oxidised) contain the group  $\text{C}-\text{O}-\text{H}$ .

<sup>1</sup> See Armstrong and Groves, *loc. cit.* pp. 812, 813.

Each of these 'alcoholic groups' itself contains the group  $\text{O}-\text{H}$ ; but the 'acid group'  $\text{H}-\text{O}-\text{C}-\text{O}$  also contains this group; now we know that the function performed by hydrogen in an alcoholic molecule is not the same as that performed by hydrogen in an acid molecule,—e.g. all, or some of the hydrogen in the latter, but none of that in the former, is replaceable by metal when the compound is acted on by a metallic carbonate,—hence we infer that the function discharged by a given atom in a molecule depends not only on the nature of that atom, but also on the nature of the atoms with which it is directly, and indirectly, connected in the molecule.

In all the alcoholic groups (viz.  $\text{H}_2\text{C}-\text{OH}$ ,  $\text{HC}-\text{OH}$ , and  $\text{C}-\text{OH}$ ) an atom of hydrogen is directly connected with an oxygen atom which is again connected with an atom of carbon, within the binding-sphere of which come either hydrogen atoms *and* atoms belonging to the other part of the molecule—always either carbon or hydrogen atoms—or only the latter. In the acid group ( $\text{O}-\text{C}-\text{OH}$ ) the carbon atom with which the hydrogen atom is indirectly connected (through an atom of oxygen) is itself directly connected with an oxygen atom, as well as with an atom, or atoms, belonging to the other part of the molecule. Now oxygen is a markedly electro-negative element; from the facts enumerated and from other similar facts, the generalisation has been made, that when an atom of hydrogen is within the binding-sphere of an atom of carbon, which also directly binds negative atoms, or negative groups of atoms, that hydrogen is, as a rule, 'replaceable by metal,' &c., i.e. that hydrogen fulfils the function of 'acid hydrogen'.

<sup>1</sup> I am aware that such expressions as are used in these paragraphs, 'a carbon atom is directly connected with,' or 'directly binds to itself, an atom of hydrogen;' 'an atom of hydrogen comes within the binding-sphere of a carbon atom,' &c., are very easily misunderstood; they appear, at first sight, to convey much more precise information than they really do convey. I have more than once insisted on the importance of clearly remembering that these and similar expressions are attempts to summarise facts concerning the actions of compounds in terms of a special theory of the structure of compounds. Nor should it be forgotten that, granting the fundamental hypotheses of the molecular theory, and also granting



75. In thus trying to use the theory of valency as a guide towards determining the structures of isomeric molecules, we have found it on the whole advantageous to limit this theory in various ways.

I. The theory is applied in strictness only to molecules of gases.

II. The valency of an atom is defined as a number which expresses the maximum number of other atoms between which and the given atom there is direct action and reaction in a molecule; this number is determined by the study of certain defined classes of molecules.

III. Isomerism is regarded as correlated with varying relative positions of atoms, not with variations in the distances between identically arranged atoms, in any molecule.

Applying the theory as thus limited, and for the most part to compounds of carbon, we found that the structural formulæ of classes of carbon compounds can be so far generalised as to admit of the assertion that the molecules of the members of any one class are characterised by the presence of a special atomic group which may be called the class-group; and that hence the first step in assigning a structural formula to a new compound is to determine, by a comparison of the reactions of this compound with those of known substances belonging to various classes, the class to which it belongs: having done this, we then eliminate from the possible structural formulæ those which do not contain the characteristic group of the class in which our compound is placed. Finally, we choose from the remaining formulæ that one which best summarises the reactions of the compound molecule under consideration and its relations to other molecules.

We found that a wide knowledge of the characters of classes of compounds is required on the part of him who would employ this method with success, and also that the chemist

that each atom can act directly on only a limited number of other atoms in a molecule, we are obliged to regard the atoms which form any molecule as performing constant but regulated movements, and not—as might be supposed by a careless, or superficial reader of the atomic explanation of isomerism—as in absolutely fixed positions within the molecule.

has constantly to be on his guard against drawing too rigid conclusions. A new compound may represent a new class, hence a new class-group has to be determined by comparing the reactions of the new compound with those of others the classification of which is fairly settled, and also by seeking to obtain other representatives of the new class. The discovery and study of new compounds apparently belonging to a known class may lead to a revision of the general formula assigned to the class, and perhaps to a division of the class into sub-classes, each characterised by its own group.

76. The application of the theory of valency to determine the most probable of many possible formulæ is evidently a matter of no little difficulty. Certain generalisations are usually adopted as guides in interpreting the results of the study of the 'chemical habitude' of molecules. The principal generalisations are these.

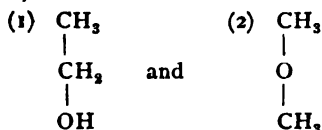
(1) 'Those atoms which are obtained as an undecomposed group in the analysis of a compound, are contained in the molecule of that compound as a group of directly combined atoms.'

(2) 'When a group of atoms passes from one compound molecule to another, the relative arrangement of these atoms is not, as a rule, altered.'

(3) 'When an atom, or group of atoms, replaces another atom or group of atoms of equal valency with itself, the replacing atom, or group, occupies (as a rule) the same position relatively to the other atoms in the molecule as was occupied by the atom, or group of atoms, which it has replaced<sup>1</sup>.'

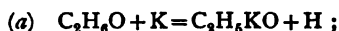
77. Many of the reactions given on pp. 144—146, as illustrative of methods for assigning structural formulæ to given compounds, also serve as illustrations of the use of these generalisations; one or two further illustrations will be given here.

Two isomerides,



<sup>1</sup> L. Meyer, *loc. cit.* pp. 252 *et seq.*

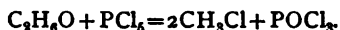
having each the formula  $C_2H_6O$  are theoretically possible<sup>1</sup>. Two compounds having this formula are known. One of these (alcohol) is acted on by potassium or sodium thus,



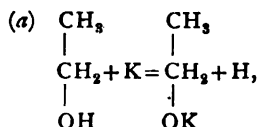
potassium (or sodium) does not act on the substance thus formed: alcohol is acted on by phosphorus pentachloride thus,



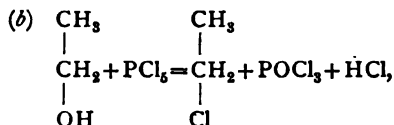
The second isomeride (methyl ether) is not acted on by potassium or sodium but reacts with phosphorus pentachloride thus,



The first formula generalises the reactions of alcohol, the second generalises the reactions of methyl ether; thus



one, and only one, hydrogen atom is represented in the formula as indirectly bound (through an oxygen atom) to a carbon atom;



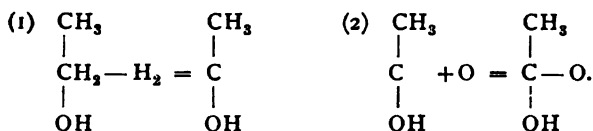
the group OH is replaced by the atom Cl, which being of equal valency is regarded as occupying the place in the molecule relatively to the other atoms, formerly occupied by the group OH.

The second formula  $H_3C - O - CH_3$  assigned to methyl ether, represents all the hydrogen atoms as directly acting on atoms of carbon, they have all the same function; but the oxygen atom is linked only to carbon, if it is replaced by two monovalent atoms, e.g. by chlorine, the molecule can no

<sup>1</sup> See Lothar Meyer, *loc. cit.* pp. 252 *et seq.*

longer hold together but separates into two molecules, each having the structure  $\text{Cl} - \text{CH}_3$ .

When the molecule  $\text{HO} - \text{CH}_2 - \text{CH}_3$  is oxidised, it loses two atoms of hydrogen, producing  $\text{C}_2\text{H}_4\text{O}$ , which is then changed, by taking up one atom of oxygen, into the new molecule  $\text{C}_2\text{H}_4\text{O}_2$ . Probably the simplest way in which these changes can be represented in structural formulæ is



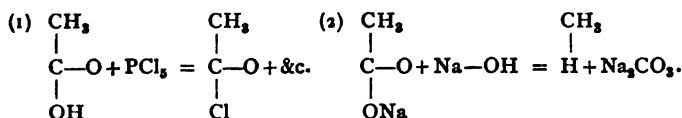
But when the molecule  $\text{C}_2\text{H}_4\text{O}_2$  is acted on by phosphorus pentachloride it yields  $\text{C}_2\text{H}_3\text{OCl}$ , and this is unacted on by the same reagent:  $\text{C}_2\text{H}_4\text{O}_2$  is a monobasic acid, when its sodium salt is heated with caustic soda it is decomposed thus,



These reactions are all expressed by the formula<sup>1</sup>  $\text{O} - \text{C} - \text{CH}_3$ ,  
 $\text{OH}$

which is therefore adopted as the structural formula for acetic acid. But when the compound  $\text{C}_2\text{H}_4\text{O}$  (intermediate between alcohol and acetic acid) is acted on by phosphorus pentachloride it yields  $\text{C}_2\text{H}_4\text{Cl}_2$ , and not  $\text{C}_2\text{H}_5\text{Cl}$  as might be expected if the formula  $\text{OH} - \text{C} - \text{CH}_3$ , provisionally assigned to it, were correct. From synthetical and analytical reactions,  $\text{C}_2\text{H}_4\text{Cl}_2$  may be shewn to be best represented by the structural formula  $\text{Cl}_2 = \text{CH} - \text{CH}_3$ ; assuming this formula, and remembering that the reaction to be explained, viz. formation of this compound from  $\text{C}_2\text{H}_4\text{O}$ , consists in the replacement of

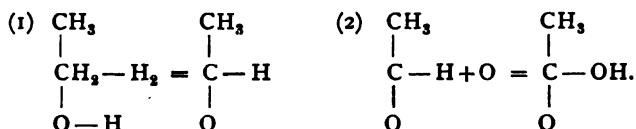
<sup>1</sup> Thus,



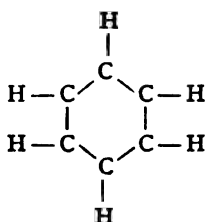
One of the carbon atoms in the original molecule remains associated with 3 atoms of hydrogen throughout both processes of change, hence we conclude that the molecule of acetic acid contains the group  $\text{CH}_3$ .

one divalent oxygen atom by two monovalent chlorine atoms, we apply generalisation (3), par. 76, and conclude that the structure of the molecule  $C_2H_4O$  is best represented by the formula  $O-CH-CH_2$ .

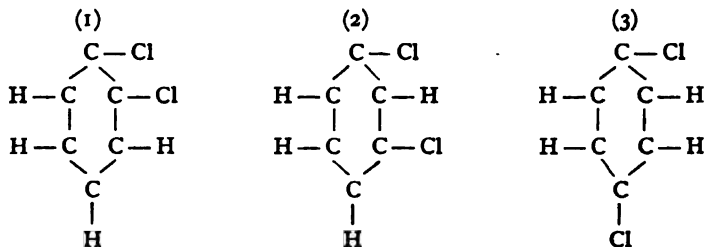
The oxidation of alcohol must then it appears be represented thus in structural formulæ,



Another and somewhat more complex illustration, taken from the so-called 'aromatic' carbon compounds, will serve to shew that the generalisations stated in par. 76, although widely applicable, must yet be used with great caution. Assuming the generally adopted structural formula for benzene<sup>1</sup> ( $C_6H_6$ ), viz.<sup>2</sup>



the existence of three, and only three isomeric dichloro- or dibromo-, &c., benzenes becomes possible, viz.



<sup>1</sup> See Armstrong and Groves, *loc. cit.* pp. 160-63; also pp. 170-74. See also *post*, pp. 163-165, par. 81.

<sup>2</sup> The fact that this formula is generally used rather than the more complex formula originally proposed by Kekulé with alternate 'doubly' and 'singly-linked'

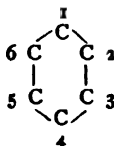
In (1) both chlorine atoms are within the binding-spheres of carbon atoms which are directly bound to one another; in (2) one carbon atom, and in (3) two carbon atoms intervene between those atoms of carbon within whose binding-spheres the chlorine atoms are found.

These three isomeric compounds are usually distinguished as 1:2, 1:3, and 1:4 dichlorobenzene; it is evident that  $1:6^1 = 1:2$ , and  $1:5 = 1:3$ . Each of these dichlorobenzenes when acted on by chlorine yields one or more isomeric trichlorobenzenes ( $C_6H_3Cl_3$ ). Körner has formulated a simple method of proving that 1:2 dichlorobenzene can yield two, 1:3 can yield three, and 1:4 can yield only one trichlorobenzene<sup>2</sup>.

Now if the generalisations we are considering are applicable to the 'aromatic' hydrocarbons, it follows that any diderivative of benzene— $C_6H_4X_2$ , where  $X$  is a monovalent atom or group of atoms—which, by a simple series of reactions can be obtained from, or can be converted into 1:2 dichloro- (or dibromo-, or dinitro-) benzene, must be itself a 1:2 derivative, i.e. the two  $X$  groups or atoms must be within the binding-spheres of carbon atoms, between which there is direct mutual action within the molecule. A similar conclusion is drawn regarding the structure of those compounds of the formula  $C_6H_4X_2$ , which can be obtained from or reduced to 1:3, or 1:4 dichloro-, &c., benzene.

carbon atoms, and that most chemists are content meanwhile to overlook the contradiction involved in employing such a formula and yet holding the theory of 'bonds,' is indicative of the unsatisfactory nature of this theory when rigidly applied.

<sup>1</sup> The carbon atoms in the hexagon are numbered thus:



<sup>2</sup> 1:2 yields 1:2:3, and 1:2:4 (1:2:3=1:2:6, and 1:2:5=1:2:4). 1:3 yields 1:2:3, and 1:3:4 (which=1:3:6), and 1:3:5. 1:4 yields 1:2:4 (which=1:3:4, =1:4:5=1:4:6). See Armstrong and Groves, *loc. cit.* pp. 267—8.

Thus 1:3 dinitrobenzene, by the action of zinc and hydrochloric acid, yields nitramidobenzene  $C_6H_4NO_2NH_2$ ; by the further action of nascent hydrogen this yields diamidobenzene  $C_6H_4(NH_2)_2$ , which, by the 'diazo reaction' (or 'Griess' reaction), yields bromohydroxybenzene  $C_6H_4Br.OH$ , this compound is therefore assumed to be a 1:3 derivative of benzene. Now when this body is fused with caustic potash it yields one of the three isomeric dihydroxybenzenes  $C_6H_4(OH)_2$ ; in accordance with generalisation (3), par. 76, this dihydroxybenzene will be regarded as a 1:3 derivative. But 1:4 bromohydroxybenzene—obtained, by a method similar to that sketched above, from 1:4 dinitrobenzene—yields, by fusion with potash, the same dihydroxybenzene as just mentioned; hence this body is now shewn to be probably a 1:4 derivative. Again, 1:4  $C_6H_4I.OH$  when fused with potash at a high temperature yields only the dihydroxybenzene in question, but at  $165^\circ$  it yields only one of the isomeric molecules<sup>2</sup>.

Another example, shewing how necessary it is to apply such generalisations as those under consideration only in a tentative manner, is furnished by some reactions of 1:4 nitro-bromobenzene ( $C_6H_4NO_2Br$ ). By the action of alcoholic ammonia on this compound nitramidobenzene ( $C_6H_4NO_2NH_2$ ) is produced; that this nitramidobenzene is, as we should expect, a 1:4 derivative can be proved by trustworthy evidence: but if the same 1:4  $C_6H_4NO_2Br$  is acted on by potassium cyanide, and the product of this action ( $C_6H_4CNBr$ ) is boiled with dilute acid, a bromobenzoic acid [ $C_6H_4Br(CO_2H)$ ] is obtained, which on account of its reactions must be regarded as a 1:3, and not a 1:4, derivative of benzene. Similarly the action of potassium cyanide followed by that of dilute acid on 1:3  $C_6H_4NO_2Br$  does not yield (as a strict application of the statement in par. 76 would lead us to expect) 1:3, but 1:2  $C_6H_4Br.CO_2H$ . And, finally, when 1:2

<sup>1</sup> For an account of these 'diazo-reactions,' which are much used in the synthesis of benzene derivatives, see Armstrong and Groves, *loc. cit.* pp. 298—9.

<sup>2</sup> See, for more details, Armstrong and Groves, *loc. cit.* pp. 521—2.

$C_6H_4NO_2Br$  is subjected to the action of potassium cyanide<sup>1</sup> no replacement of  $NO_2$  by  $CN$  occurs<sup>2</sup>.

78. The application of the theory of valency to the phenomena summed up in the term isomerism has rendered more definite that general conception of the molecule as a structure which arose so soon as it was recognised that each atom in a molecule could act directly on a limited number of other atoms. Analyses of reactions, and comparisons of classes of reactions, have led to the adoption of certain rules which, when applied with caution, have proved of very considerable service in researches on molecular structure. These researches have served to emphasise the fundamental connection which exists between composition and properties, between function and quality of material: but chemistry is not now contented with connecting the reactions of compounds with their elementary composition, or even with the atomic composition of their molecules, she attempts, and is gradually succeeding in the attempt, to connect certain definite arrangements of atoms in molecules with certain definite properties and actions of these molecules.

79. In his remarkable paper published in 1858, Kekulé recognised that the function performed by an atom in any molecule depends on the nature of the other atoms, as well as on the nature of the given atom, and also on the arrangement of all the atoms. Since 1858 the nature of the dependence in question has been more fully elucidated; and although it cannot be said that we have at present much knowledge, capable of being generalised in statements at once accurate and wide, of the connections between the functions of parts of molecules and the atomic composition and structure of

<sup>1</sup> In Armstrong and Groves, *loc. cit.* pp. 334—6 will be found an account of the action of potassium cyanide on benzene derivatives; this action, although abnormal, may be expressed by a tolerably simple generalisation.

<sup>2</sup> Further examples of the point under discussion will be found in the change of normal propyl to isopropyl, by (1) action of  $Al_2Br_6$  [see Kekulé, *Ber.* 12. 2279] or (2) action of zinc dust [see Jacobsen, *Ber.* 12. 1512]; also in the change of  $C_nH_{2n+2}CN$  to  $C_nH_{2n+2}NC$  by the action of heat: and also in the action of reducing agents on phenanthraquinone [see Japp, *C. S. Journal Trans.* for 1883. 13, note].



these molecules, yet we are certainly gathering facts which will doubtless prove the basis for far-reaching generalisations.

Numerous illustrations have already been given of the existence of a connection of some kind between the functions of parts of a molecule and the composition, using this term in its widest sense, of the whole molecule. But the fact of the existence of such a connection is so important that I wish to devote a paragraph to its illustration.

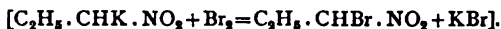
The relation to be illustrated is that between the function performed by an atom, or atomic group, in a molecule,

and  $\left\{ \begin{array}{l} \text{I. The nature, and arrangement, relatively} \\ \text{to the given atom (or group), of the} \\ \text{other atoms,} \\ \text{II. The general relative arrangement of all} \\ \text{the parts,} \end{array} \right\} \text{ in the molecule.}$

80. I. That the function performed by an atom of hydrogen in a molecule varies according to the nature and arrangement relatively to the hydrogen of the other atoms, has already been shewn (see par. 74, pp. 147—149). Hydrogen which is associated with negative atoms or groups is as a rule 'replaceable by metals,' in other words, performs acid functions in the molecule. Thus of the two compounds, potassium-nitropropane and bromo-nitropropane, the latter is much more decidedly acid than the former: if the formulæ are compared,



<sup>1</sup> The reaction of formation of bromo-nitropropane affords a very interesting example of the modifying influence of one atom on another in a molecule: bromine does not replace hydrogen in nitropropane, but when an atom of hydrogen in the nitropropane molecule is replaced by potassium, the product is readily acted on by bromine with substitution of an atom of the very positive potassium by an atom of the very negative bromine



(See Armstrong and Groves, *loc. cit.* pp. 166—7.)

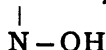
it is seen that, in the markedly acid compound, the carbon atom with which the sixth atom of hydrogen is represented as directly connected is itself directly bound to the negative group  $\text{NO}_2$ , and to the negative atom  $\text{Br}$ ; but that, in the less acid compound, this carbon atom is represented as directly bound to the negative group  $\text{NO}_2$ , and to the positive atom  $\text{K}$ .

Again  $\text{C}-\text{H}$  is not an acid, but  $\text{C}-\text{H}$  is; the influence



of the very negative  $\text{NO}_2$  group seems to be impressed through the carbon atom on the hydrogen atom of the molecule.

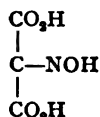
In these cases the atom of 'acid hydrogen' is represented as *directly* bound to a carbon atom within the binding-sphere of which come negative atoms or groups. But the case of the nitrolic acids, assuming the usually accepted formula, viz.  $(\text{C}_n\text{H}_{n+1})-\text{C}-\text{NO}_2^1$ , to be correct, shews that



an atom of hydrogen which is *indirectly* bound to carbon itself binding negative groups may react as acid hydrogen. Glyoxaline and tribromoglyoxaline also furnish examples in point; each of these molecules contains one atom of acid hydrogen<sup>2</sup>.

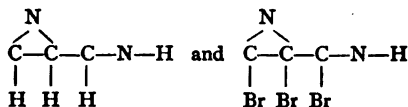
A portion of the hydrogen in monohydric alcohols is replaceable by metal, but only by the very positive metals, e.g.

<sup>1</sup> It is interesting to note that iso-nitroso malonic acid



acts as a dibasic, *not tribasic*, acid.

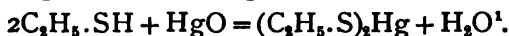
<sup>2</sup> The most probable formulæ are,



(see Armstrong and Groves, *loc. cit.* p. 769). Some reactions of water are consistent with the statement that one of the hydrogen atoms performs the functions of acid hydrogen; e.g.



$C_2H_5.OH + K = C_2H_5.OK + H$ ; but by the introduction of an atom of sulphur in place of oxygen a thio-alcohol is obtained which readily exchanges hydrogen even for comparatively negative metals, e.g.



Again, the experiments of R. Meyer<sup>2</sup> appear to prove that an atom of hydrogen in the molecule of a carbon compound can be replaced by the group OH, by the action of oxidising agents, only when the carbon atom with which the hydrogen is directly connected does not directly bind any other hydrogen atoms; thus isobutyric acid is oxidised by potassium permanganate to isohydroxybutyric acid, but normal butyric acid yields acetic, oxalic, carbonic and other acids under the same conditions.

[In structural formulæ,  $H_3C-CH_2-CH_2-C \begin{smallmatrix} O \\ \diagup \\ OH \end{smallmatrix}$  does not yield an hydroxy-acid; but  $\begin{smallmatrix} O \\ \diagup \\ HO \end{smallmatrix} C-CH \begin{smallmatrix} CH_3 \\ \diagup \\ CH_3 \end{smallmatrix}$  yields  $\begin{smallmatrix} O \\ \diagup \\ HO \end{smallmatrix} C-CH \begin{smallmatrix} CH_3 \\ \diagup \\ COH \\ \diagdown \\ CH_3 \end{smallmatrix}$ .]

Victor Meyer's experiments likewise appear to establish a connection between the structure of the nitro-derivatives of compounds of the general form  $X-CH-X$  (produced by the action of  $NO.OH$  on those compounds) and the relatively easy or difficult removal, in whole or in part, of one of the  $X$  groups<sup>3</sup>.

Further illustrations of the connections between the functions of parts of molecules and the nature and arrangement of the other parts are furnished by the reactions of (a) the nitro-derivatives of benzene and its homologues<sup>4</sup>, (b) chloro- and

<sup>1</sup> For details concerning these reactions see Armstrong and Groves, *loc. cit.* pp. 660—1.

<sup>2</sup> *Ber.* 11. 1787: 12. 2238; *Annalen*, 219. 234: 220. 1; see also J. BREDT, *Ber.* 13. 748.

<sup>3</sup> *Ber.* 16. 610.

<sup>4</sup> Armstrong and Groves, *loc. cit.* pp. 322—5.

chloro-nitrobenzenes<sup>1</sup>, and (c) benzoquinone and chloro-benzoquinone<sup>2</sup>.

(a) Two hydrogen atoms in the benzene molecule  $C_6H_6$  can be replaced by the group  $NO_2$  twice, only by the action of very concentrated nitric acid mixed with concentrated sulphuric acid; if however an atom of hydrogen in  $C_6H_6$  is replaced by the group  $CH_3$ , the resulting molecule— $C_6H_5.CH_3$ —is much more readily converted into the dinitro-derivative  $C_6H_5(NO_2)_2.CH_3$ ; if three hydrogen atoms in  $C_6H_6$  are replaced by  $CH_3$  three times, the molecule thus formed,  $[C_6H_3(CH_3)_3]$  *very easily* yields a trinitro-derivative  $C_6(NO_2)_3(CH_3)_3$  by the action of nitric acid.

(b) The chloro-benzenes,  $C_6H_{6-x}Cl_x$ , do not readily exchange chlorine for other atoms; but the chloro-nitrobenzenes, as a class, by mere contact with ammonia yield amido-nitrobenzenes, e.g.  $C_6H_4ClNO_2$  exchanges Cl for  $NH_2$ , yielding  $C_6H_4(NH_2)NO_2$ . Although the action of ammonia on the chloro-nitrobenzenes generally results in the exchange of chlorine atoms for the group of atoms  $NH_2$ , nevertheless one of the isomeric molecules represented by the formula  $C_6H_2Cl_2(NO_2)_2$  yields  $C_6H_2Cl_2NO_2(NH_2)$  by the action of ammonia upon it; and similarly one of the isomeric bromo-trinitrobenzenes,  $C_6H_2Br(NO_2)_3$ , exchanges, not its Br atom, but one of the  $NO_2$  groups, for  $NH_2$ , under the action of the same reagent. Again, although the homologues of benzene readily yield either chloro- or nitro-derivatives, and the chloro-derivatives may be readily nitrated, yet hydrogen in nitro-derivatives is not easily replaced by chlorine.

(c) When benzene ( $C_6H_6$ ) is oxidised, benzoquinone ( $C_6H_4O_2$ ) is probably produced but decomposed again; the chemical change proceeds further than formation of benzoquinone. If however benzene is acted on by oxidising and chlorinating reagents simultaneously, dichlorobenzoquinone ( $C_6H_2Cl_2O_2$ ) is formed and can be isolated. The substitution of chlorine for hydrogen in the  $C_6H_6$  molecule modifies the function of part of the remaining hydrogen so that it can be

<sup>1</sup> Armstrong and Groves, *loc. cit.* pp. 333—4.

<sup>2</sup> *Ibid.* *loc. cit.* p. 794.

replaced by oxygen, and at the same time the presence of  $\text{Cl}_2$  in place of  $\text{H}_2$  in the new molecule appears to confer on it a greatly increased stability towards oxidising substances.

81. II. A good illustration of the influence exerted by the arrangement of all the atoms in a molecule on the functions of one, or some, of these atoms, is afforded by a comparative study of the two groups of carbon compounds—more especially the hydrocarbons—generally known as ‘fatty’ (or ‘paraffinoid’) and ‘aromatic’ (or ‘benzenoid’) respectively<sup>1</sup>: a few, but only a few, of the more important points will be briefly stated.

Comparing the action of concentrated nitric or sulphuric acid on a paraffin, e.g.  $\text{C}_2\text{H}_6$ , with the action of the same acid on a benzene, e.g.  $\text{C}_6\text{H}_6$ , it is noticed that while one or more hydrogen atoms in the molecule of the latter are readily replaced by the group  $\text{NO}_2$  or  $\text{SO}_3\text{H}$ , the acid is without action on the former hydrocarbon. When the homologues of benzene are oxidised they, as a class, yield quinones, the molecule of any one of which contains the same number of carbon atoms as the parent hydrocarbon, but has two atoms of oxygen in place of two atoms of hydrogen in the original molecule. When the paraffinoid hydrocarbons, on the other hand, are oxidised, they do not yield derivatives analogous to the quinones, but rather afford mixtures of acids the molecule of each of which contains a smaller number of carbon atoms than were present in the original hydrocarbon molecule.

When chlorine acts on the molecule of a paraffinoid hydrocarbon containing only tetravalent<sup>2</sup> carbon atoms, it produces chloro-substitution derivatives containing tetravalent carbon atoms, the whole of the hydrogen in the hydrocarbon being eventually replaced by chlorine, the further action of chlorine then frequently results in a separation of the molecule into two or more molecules, each containing a smaller number of carbon atoms than the original molecule. When however chlorine acts on the molecule of a paraffinoid

<sup>1</sup> See Armstrong and Groves, pp. 391—402.

<sup>2</sup> In ordinary nomenclature it would be said ‘singly-linked carbon atoms.’

hydrocarbon containing two or more trivalent<sup>1</sup> carbon atoms it generally combines with it and so produces a molecule containing tetravalent carbon atoms, which is then acted on by chlorine as hydrocarbons with tetravalent carbon atoms usually are.

Thus,  $\text{H}_2\text{C}-\text{CH}_2-\text{CH}_2$ , by the action of  $\text{ICl}$  gives  $\text{H}_2\text{C}-\text{CH}_2-\text{CH}_2\text{Cl}$  &c., and finally  $\text{Cl}_2\text{C}-\text{CCl}_2-\text{CCl}_2$ , and this octochloropropane by the continued action of  $\text{ICl}$  gives  $\text{Cl}_2\text{C}-\text{CCl}_2$  and  $\text{CCl}_4$ ; but  $\text{H}_2\text{C}-\text{CH}_2-\text{CH}_2$ , containing two trivalent carbon atoms, by the action of  $\text{ICl}$  gives  $\text{ClH}_2\text{C}-\text{CH}_2-\text{CH}_2\text{Cl}$ , containing only tetravalent carbon atoms, by the further action of  $\text{ICl}$ ,  $\text{C}_2\text{Cl}_6$  is obtained, and this is eventually decomposed to  $\text{C}_2\text{Cl}_4$  and  $\text{CCl}_4$ .

The action of chlorine on the aromatic hydrocarbon benzene ( $\text{C}_6\text{H}_6$ ) finally results in the formation of hexchlorobenzene  $\text{C}_6\text{Cl}_6$ , in which, it may be safely asserted from the formula and from a study of the properties of the compound, the carbon atoms act on, and are acted on by, the same number of atoms as in the original  $\text{C}_6\text{H}_6$  molecule. So far then benzene behaves like a paraffin; but  $\text{ICl}$  has no action on  $\text{C}_6\text{Cl}_6$ , the molecule refuses to separate into parts, the six atoms of carbon are apparently more firmly joined together, and form a more stable group, than the carbon atoms in the molecule of a paraffin.

The functions both of the hydrogen and carbon atoms in the molecules of a benzene and of a paraffin—say in  $\text{C}_6\text{H}_6$  and in  $\text{C}_6\text{H}_{14}$ —evidently depend to some extent on the general arrangement of all the atoms in these molecules.

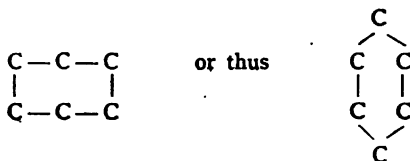
The arrangement of carbon atoms supposed to characterise the molecule of a fatty hydrocarbon, e.g. a paraffin, is usually spoken of as arrangement in '*an open chain*,' while that supposed to characterise the molecule of an aromatic hydrocarbon, e.g. a benzene, is called '*a closed ring*'<sup>2</sup>. If the action

<sup>1</sup> In ordinary nomenclature it would be said 'doubly-linked carbon atoms.'

<sup>2</sup> Ring-formed molecules resemble unsaturated molecules in that they can directly combine with monovalent atoms without loss of any of their constituent atoms (e.g. benzene forms  $\text{C}_6\text{H}_5\text{Cl}$ ); but they resemble saturated molecules in that the assumption of monovalent atoms is possible only when preceded by a

between atom and atom be supposed to begin at one of the carbon atoms, then in a *closed ring* molecule it returns to that atom; in other words each carbon atom acts on, and is acted on by, at least two other carbon atoms in the molecule: but in an *open chain* molecule the action does not return to the carbon atom at which it started; in other words, there are two carbon atoms in the molecule, each of which acts on, and is acted on by, only one other carbon atom.

The *ring-formed* molecule containing six carbon atoms may be represented thus,



and the *open chain* molecule thus:



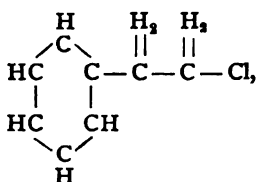
As the six carbon atoms in the molecule of benzene appear to form a very stable group, they are sometimes spoken of as the '*six-carbon-nucleus*' of the molecule. Now if the monochloro-derivative of xylene ( $\text{C}_8\text{H}_{10}$ ) produced by the action of chlorine on that hydrocarbon when cold is compared with the monochloro-derivative produced by the action of chlorine on the same hydrocarbon when hot, it is found that the latter readily exchanges its chlorine atom for the group OH with production of an alcohol ( $\text{C}_8\text{H}_9(\text{OH})$ ), but that the chlorine atom in the former can scarcely be replaced by other radicles. If we assume the ordinarily accepted structural formulæ for the two isomeric monochloroxylenes we at once

rearrangement of the mutual actions between some of the polyvalent atoms (see e. g. formula of benzene on p. 154). (*Lossen.*)

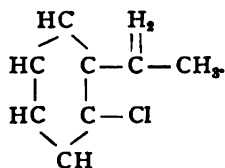
The number of molecules produced in any reaction wherein only saturated molecules take part is equal to or greater than the number of molecules taking part in the reaction: when the number produced in any reaction is smaller than the number of molecules originally taking part in the reaction, at least one of the reacting molecules must be either unsaturated or ring-formed. (*Lossen.*)

It is evident that a ring-formed molecule must contain at least three polyvalent atoms, and that for such molecules  $n_1 < n_2 + 2n_3 + \&c. \dots + 2$ .

see how profoundly the functions of the chlorine atoms depend on the relative arrangement of all the atoms in the molecule. The formulæ in question are (a) monochloroxylylene from *hot* xylene,



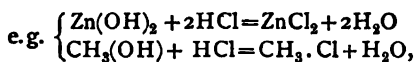
(b) monochloroxylylene from *cold* xylene,



The chlorine atom in (a) is said to be in '*the side chain*,' and in (b) in the '*central nucleus*.' In the hydrocarbon  $\text{C}_8\text{H}_{10}$  we have the properties both of a paraffin and a benzene; part of the molecule, the six-carbon-nucleus, behaves as a benzenoid molecule; the other part, the side chain ( $\text{C}_2\text{H}_5$ ) as a paraffinoid molecule.

A comparison of some of the reactions of metallic hydroxides, alcohols, and phenols, will serve to illustrate the dependence of the functions of part of a molecule, at once on the nature and arrangement (relatively to this part) of the other atoms, and also on the general arrangement of all the atoms, in the molecule.

The action of acids on metallic hydroxides and alcohols results in the formation of salts;



but phenols do not yield analogous products by this reaction. Alcohols and some metallic hydroxides—e.g.  $\text{Zn(OH)}_2$  and  $\text{Al}_2(\text{OH})_6$ —yield unstable metallic derivatives by the action of markedly positive metals or their hydroxides; phenols however yield much more stable metallic derivatives by the action of the



same metals, their hydroxides or carbonates. The hydrogen atom (or atoms) which is indirectly connected, through oxygen, with the metal or hydrocarbon-radicle of these molecules, evidently fulfils more or less acid or basic functions, according to the nature of the other part of the molecule. When that other part is a metallic atom (or atoms) the hydrogen is as a rule 'basic,' but in certain cases it is also feebly acid; when the nonhydroxylic part of the molecule is composed of carbon and hydrogen atoms arranged in an 'open chain,' the hydrogen appears to be analogous to the hydrogen of metallic hydroxides, and when the carbon and hydrogen are arranged in a 'closed ring' the hydrogen appears to be more distinctly acid in function<sup>1</sup>.

The following facts and generalisations concerning the action of reagents on various benzene derivatives afford further examples of the influence exerted by relative position, and nature of parts of a molecule, and general arrangement of all atoms in a molecule, on reactions wherein atoms (or atomic groups) in the molecule are substituted by other atoms or groups.

In the production of certain disubstituted derivatives of benzene,  $C_6H_4XX'$ , from monosubstituted derivatives,  $C_6H_5X$ , it is found that whether the diderivative shall belong to the 1 : 2, 1 : 3, or 1 : 4 series<sup>2</sup>, depends on the nature of the atom, or atomic group  $X$ , in  $C_6H_5X$ , and also on the nature of the atom, or group  $X'$ , in  $C_6H_4XX'$ . When  $X = Cl, Br, I, OH, CH_3$  or  $NH_2$ , and  $X' = Cl, Br, I, NO_2$  or  $SO_3H$ , the diderivative  $C_6H_4XX'$  generally belongs to the 1 : 4 series; when  $X = NO_2, SO_3H$  or  $CO_2H$ , and  $X' = Cl, Br, I, NO_2$  or  $SO_3H$ , then  $C_6H_4XX'$  generally belongs to the 1 : 3 series<sup>3</sup>.

Derivatives of benzene containing paraffinoid radicles as 'side chains,' when oxidised, yield mono-, di-, tri-, &c., basic acids, according to the number of side chains in the original molecule; thus  $C_6H_4.C_2H_5.CH_3$  yields  $C_6H_4(CO_2H)_2$ ,  $C_6H_4.CH_3.CO_2H$  also yields  $C_6H_4(CO_2H)_2$ , &c., but if a

<sup>1</sup> See Armstrong and Groves, *loc. cit.* p. 566.

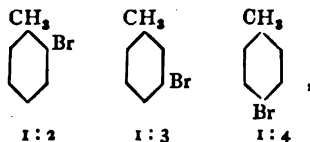
<sup>2</sup> See par. 77, p. 155 for an explanation of this notation.

<sup>3</sup> See table in Armstrong and Groves, *loc. cit.* p. 337.

negative atom or group is introduced into the benzene derivative and the oxidation is then effected, the paraffin-radicle which forms the side chain nearest to<sup>1</sup> the negative atom (or group) is protected by that atom (or group) and does not undergo oxidation. Thus  $C_6H_4 \cdot CH_3 \cdot C_2H_5$  [1:4] when oxidised produces  $C_6H_4(CO_2H)_2$ , but  $C_6H_5 \cdot Br \cdot CH_3 \cdot C_2H_5$  [1:2:4] produces  $C_6H_5Br \cdot CH_3 \cdot CO_2H$  [1:2:4]. So again  $C_6H_4(C_2H_5)_2$  [1:4] oxidises to  $C_6H_4(CO_2H)_2$ , but  $C_6H_5 \cdot C_2H_5 \cdot SO_2NH_2 \cdot C_2H_5$  [1:2:4] oxidises to  $C_6H_5 \cdot C_2H_5 \cdot SO_2NH_2 \cdot CO_2H$  [1:2:4], in this case the  $C_2H_5$  nearest to the negative group is protected, while the other  $C_2H_5$  group undergoes oxidation to  $CO_2H$ <sup>2</sup>. So also if 1:3:4, 1:4:5 or 1:2:4 dimethylnitroxyline ( $C_6H_7 \cdot CH_3 \cdot CH_3 \cdot NO_2$ ) is oxidised, in each case the  $CH_3$  group nearest to the  $NO_2$  group is unchanged, and the other  $CH_3$  group is oxidised to  $CO_2H$ ; but if the 1:3:5 dimethylnitroxyline is oxidised, both the  $CH_3$  groups are converted into  $CO_2H$  groups; now in a 1:3:5 derivative the substituting groups are equally distributed, in the case before us each methyl group is situated in exactly the same position relatively to the  $NO_2$  group<sup>3</sup>.

Once more, by the action of chlorine or bromine on aniline, trichlor- or tribromaniline is produced: when 1:2 or 1:4 monochlor- monobrom- or mononitr aniline is chlorinated, 2 atoms of chlorine are taken up by the molecule in place of 2 atoms of hydrogen; when 1:2 or 1:4 dichlor- &c. aniline is chlorinated, one atom of chlorine is taken up, so that in every case the total number of negative atoms in the molecule is 3,

<sup>1</sup> 'Nearest to;' compare the structural formulæ for the three methylbromobenzenes



the Br atom is said to be nearer to the  $CH_3$  group in the 1:2 than in the 1:3, and nearer in the 1:3 than in the 1:4.

<sup>2</sup> See Remsen and Hall, *Amer. Chem. Journal* 2. 50; and Remsen and Noyes, *loc. cit.* 4. 197.

<sup>3</sup> See E. Wroblewsky, *Ber.* 15. 1021.

which is also the number of negative atoms that can be substituted for hydrogen in the molecule of aniline itself. But when 1:3 monochlor-, &c. aniline is chlorinated, 3 atoms of chlorine are substituted for 3 of hydrogen, and when 1:3 dichlor-, &c. aniline is chlorinated 3 atoms of chlorine are still taken up. Thus

$C_6H_5.NH_2$  by chlorination yields  $C_6H_2Cl_3.NH_2$ ,

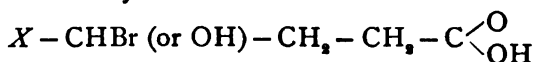
1:2 or 1:4  $C_6H_4Cl.NH_2$  yields  $C_6H_2Cl_3.NH_2$

1:2 or 1:4  $C_6H_3Cl_2.NH_2$  yields  $C_6H_2Cl_3.NH_2$

but 1:3  $C_6H_4Cl.NH_2$  yields  $C_6HCl_4.NH_2$

and 1:3  $C_6H_3Cl_2.NH_2$  yields  $C_6Cl_5.NH_2$ .<sup>1</sup>

Another interesting example of the connection we are considering is furnished by the *lactones*, under which name are included several compounds obtained by removing the elements of water from hydroxy-acids, or the elements of hydrobromic acid from bromo-acids: thus hydroxycaproic acid  $C_6H_{10}(OH).CO_2H$  yields the lactone  $C_6H_{10}CO_2$ , and bromo-valeric acid  $C_4H_8Br.CO_2H$  the lactone  $C_4H_8CO_2$ . Researches by Fittig<sup>2</sup> and others shew that lactones are formed only from those acids in the molecules of which two OH groups, or a halogen atom and an OH group, are directly connected with atoms of carbon which are themselves connected indirectly through two other carbon atoms; thus, an acid represented by the formula  $X-CHBr$  (or  $OH$ )  $-CH_2-C \begin{smallmatrix} O \\ \diagup \\ OH \end{smallmatrix}$  does not form a lactone, but when acted on by water and bases tends to produce an unsaturated acid; on the other hand an acid represented by the formula



readily forms a lactone the constitution of which is probably represented by the formula  $X \underline{CH-CH_2-CH_2-C \begin{smallmatrix} O \\ \diagup \\ OH \end{smallmatrix}}$ .

Reference may also be made to the connection between

<sup>1</sup> See C. Langer, *Ber.* 15. 1061 and 1328.

<sup>2</sup> See R. Fittig, *Annalen*, 200. 21: 208. 111; also J. Bredt, *Ber.* 13. 748; also E. Hjett, *Ber.* 15. 629.

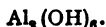
the structure of the olefines ( $C_nH_{2n}$ ) and that of the additive compounds obtained from them by the action of  $HX$  ( $X = Cl, OH \&c.$ ); and this connection may be compared with that existing between the structures of the haloid derivatives of the olefines and the additive compounds obtained by the action on these holoid derivatives of  $HX^1$ .

82. From these considerations it would appear that the readiness to undergo this reaction or that, or, as might be said, the *chemical stability* of a molecule, depends largely on the balance of properties of parts of the molecule, such balance being itself connected with the nature and relative arrangements of these parts. Many of the reactions cited in the foregoing paragraphs (80 and 81) may serve as illustrations of the meaning of the expression 'chemical stability', and of the conception of a dependence between this and the balance of functions of parts of the molecule; let one more illustration suffice.

The conditions under which an atom of hydrogen apparently fulfils alcoholic functions have been already summarised [pp. 165—166]. In some molecules the acid and alcoholic functions of the hydrogen atoms seem to be equally balanced, so that for some purposes the compound may be classed as an alcohol, for other purposes as an acid; thus, when an atom of hydrogen in the benzene molecule,  $C_6H_6$ , is replaced by the group  $OH$ , the product— $C_6H_5.OH$ —exhibits many of the properties of an acid and also many of the properties of an alcohol, e.g. a hydrogen atom is replaceable by metal when the compound is acted on by alkali metal or alkaline hydroxide, but not when it is acted on by an alkaline carbonate<sup>2</sup>. By replacing three hydrogen atoms in the phenol molecule—( $C_6H_5.OH$ )—by  $NH_2$  and  $NO_2$  groups, compounds are obtained which exhibit both basic and acid properties, e.g. the molecule  $C_6H_2.(NH_2)_2.(NO_2)_2.OH$  combines with the molecule  $HCl$ , but the product is not very stable; the same molecule however readily exchanges an atom of hydrogen for metal by

<sup>1</sup> See Armstrong and Groves, *loc. cit.* pp. 181 and 200.

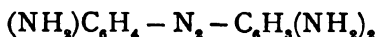
<sup>2</sup> In these actions phenol presents an analogy to aluminium hydroxide—



the action of alkaline carbonates, thus forming well marked stable metallic derivatives—e.g.  $C_6H_5(NH_2)(NO_2)ONa$ .

If however two  $NH_2$  groups and one  $NO_2$  group are introduced in place of three hydrogen atoms in the phenol molecule, the product  $C_6H_3(NH_2)_2(NO_2)OH$  is distinctly basic, combining readily with  $HCl$ , but yielding only unstable metallic derivatives.

83. Not only is the general chemical stability of a molecule dependent, in part, on the balance of functions of the atoms and atomic groups in the molecule, but many of the properties generally called physical are correlated with a similar balance of parts. Thus Witt<sup>1</sup> has shewn that there exists a definite connection between the tinctorial properties of many derivatives of azobenzene ( $C_6H_5-N_2-C_6H_5$ ) and the atomic composition and structure of these molecules. By introducing the group  $NH_2$  in place of hydrogen in the azobenzene molecule, salt-forming molecules are produced, possessed of considerable dyeing properties; if negative groups, as  $OH$ ,  $HSO_3$ , &c. are introduced into the molecule the products are also strongly coloured, but the best dyes are formed by the introduction of both basic and acid groups. Thus  $C_6H_5-N_2-C_6H_4(NH_2)$  dyes a light yellow but the colour is very fugitive; the colour of



is too dull; but  $C_6H_5-N_2-C_6H_3(NH_2)_2.HCl$  acts as a beautiful reddish dye; the compound whose composition is represented by the formula  $(NH.C_6H_5)C_6H_4-N_2-C_6H_4(SO_3H)$  also forms an extremely good dye, in this molecule, the basic and acid functions are nearly balanced.

We have already learned (pars. 32—35) that a general relation exists between the crystalline form of a compound and the number and arrangement of the atoms in the molecule of that compound. Groth<sup>2</sup>, and others, have shewn that the

<sup>1</sup> *C. S. Journal Trans.* for 1879. 179, 357.

<sup>2</sup> *Pogg. Ann.* 141. 31. See also C. Hintze, *Pogg. Ergbd.* 6. 195; C. Bodewig, *Pogg. Ann.* 158. 239; P. Friedländer, *Zeitschr. Krystall.* 3. 168; and the article 'Isomorphie' in the *Neues Handwörterbuch der Chemie*, 3. especially pp. 854—9.

substitution of Cl, Br,  $\text{NO}_2$ , or OH &c., for hydrogen in the molecule of benzene derivatives is accompanied by definite changes in the crystalline forms of the compounds. The relations existing between crystalline form and chemical structure, so far as the latter is modified by processes of substitution, are called by Groth *morphotropic* relations. The change of crystalline form in any given case depends on (1) the chemical nature of the parent substance, (2) the crystalline system to which it belongs, (3) the chemical nature of the substituting atom (or group) and (4) the chemical nature of the product of the reaction, using the expression 'chemical nature' in its widest sense as including the conceptions of atomic composition and atomic structure.

When the parent substance belongs to a crystalline system in which the relations of the axes are not invariable, substitution of Cl, Br, &c., generally only produces changes in these relations, without total changes to other systems; but if the parent substance belongs to the regular system, the substituted product is found to belong to one of the other five systems.

Groth's researches lead to the following generalisations concerning the derivatives of benzene:—

(1) Substitution of H by OH, or  $\text{NO}_2$ , is accompanied by changes in the relations of the axes, but not by changes from one system to another.

(2) Substitution of H by Cl or Br, is accompanied by changes from one crystalline system to another, less symmetrical, system; but further substitution of the same atoms is sometimes accompanied by a return to a more symmetrical system.

(3) Substitution of H by  $\text{CH}_3$ , is also accompanied by marked changes in crystalline symmetry.

Chemically similar derivatives of benzene belonging to a *para* [1 : 4] series shew greater crystallographic analogy with one another than with the members of a *meta* [1 : 3] or an *ortho* [1 : 2] series. This statement, when rendered more definite by extended investigations, will doubtless lead to important generalisations connecting crystalline form with atomic arrangement; meanwhile it may be tentatively applied in some of

the problems presented by isomorphism. Thus, 1:3 dinitrobenzene on nitration yields a certain trinitrobenzene; to which of the three series of benzene-derivatives does this trinitro-compound belong<sup>1</sup>? If the formulæ of the possible trinitrobenzenes are compared with those of the three dinitrobenzenes it will be found that 1:2 dinitro- can yield 2 trinitrobenzenes, (viz. 1:2:3, and 1:3:4), 1:3 dinitro- can yield 3 trinitrobenzenes, (viz. 1:2:3, 1:3:4, and 1:3:5), and 1:4 dinitro- can yield only one trinitrobenzene (viz. 1:3:4.) Of the three possible trinitrobenzenes, the 1:3:4 is obtainable from each of the three dinitro-compounds, the 1:2:3 is obtainable from either the 1:2 or the 1:3 dinitro-compound, but the 1:3:5 is obtainable from the 1:3 dinitro-compound only.

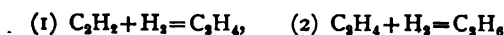
Now let us distinguish the crystalline form of the trinitrobenzene, a formula for which is to be found, by the symbol  $\square$ . The compound in question is obtained from the 1:3 dinitrobenzene; if it is the 1:3:4 compound, then a trinitrobenzene having the symbol  $\square$  should be obtained from each of the other dinitrobenzenes, if it is the 1:2:3 compound, then a trinitrobenzene having the symbol  $\square$  should be obtained from 1:2 but not from 1:4 dinitrobenzene. But experiment shews that one and only one trinitrobenzene, the crystalline form of which we have designated by  $\square$ , is obtainable; hence the conclusion is that the compound in question is 1:3:5 trinitrobenzene.

The general conclusion to be drawn from these facts is, that, in some compounds at any rate, crystalline form is more or less closely connected with the nature and arrangement of the atoms and groups of atoms in the compound molecules.

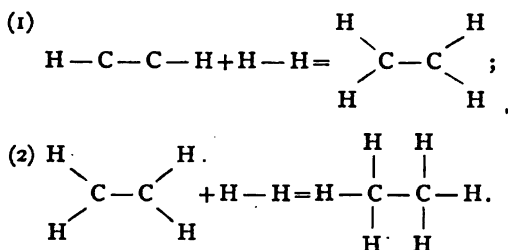
84. Very many measurements have been made of the quantities of heat evolved or absorbed during processes of chemical change: this subject will be considered in detail in a future chapter; at present I wish to insist on the fact that the data of thermal chemistry establish an undoubted connection between the thermal changes which accompany chemical reactions and the nature and arrangement of the atoms, and groups of

<sup>1</sup> See 'Isomorphie,' *loc. cit.* p. 858.

atoms, in the molecules which take part in these reactions. Especial reference must here be made to the experiments of J. Thomsen<sup>1</sup>, from which that naturalist has drawn the conclusion that it is possible to assign a definite thermal value to the atomic transaction expressed in the language of the theory of valency as 'change from acting as a divalent to 'acting as a trivalent carbon atom,' or 'from acting as a 'trivalent to acting as a tetravalent carbon atom.' Thus, representing the changes



in structural formulæ we have

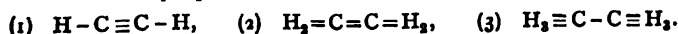


Now Thomsen seeks to separate the thermal change accompanying the addition of  $\text{H}_2$  to  $\text{C}_2\text{H}_2$ , or to  $\text{C}_2\text{H}_4$ , from that which he supposes to accompany the change of divalent into trivalent, or trivalent into tetravalent carbon atoms. Thomsen does not himself put the statement of what he wishes to do in this form; he uses the language of the theory of bonds; he calculates the 'heats of formation' of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , and  $\text{C}_2\text{H}_6$ , i.e. of hydrocarbon molecules containing (1) a pair of 'trebly-linked' carbon atoms, (2) a pair of 'doubly-linked,' and (3) a pair of 'singly-linked' carbon atoms<sup>2</sup>. By

<sup>1</sup> *Ber.* 13. 1321, and *Journal für prakt. Chemie.* 23. 157 and 163. See also *post.* chap. IV., par. 134.

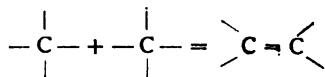
<sup>2</sup> 'Heat of formation' of a compound = difference between heat evolved during complete combustion of the elementary constituents of the compound, and heat evolved during complete combustion of the compound itself, stated in thermal units per formula-weight of the compound. (See chapter IV., par. 120.)

<sup>3</sup> The bond theory represents the molecules in question thus:

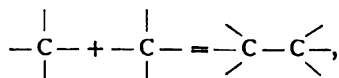




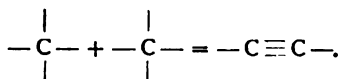
making many assumptions, concerning the structure of the molecule of carbon, and the amounts of heat absorbed in separating carbon and hydrogen molecules into atoms, &c., Thomsen deduces certain thermal values for the 'satisfaction 'of each bond,' or affinity, of the carbon atom by a bond, or affinity, of another carbon atom. The thermal values thus obtained differ, according to Thomsen, for each bond; in other words the quantity of heat evolved during the satisfaction of bond *a* is different from that evolved during the satisfaction of bond *b*, which quantity again is not the same as that accompanying the satisfaction of bond *c*. Or we may put the matter thus,—the thermal value of the theoretically occurring transaction



is not double the value of the other transaction



nor is the latter of these represented by one-third of the thermal value of the transaction



Indeed Thomsen arrives at the conclusion, strange when stated in the language of the bond theory, that 'the treble-linking of two atoms of carbon is accompanied by no 'thermal change.'

It seems to me that Thomsen's conclusions when stated in the terminology of the theory of bonds oblige one to say either that this theory is meaningless, or that Thomsen's results are absurd; for, a 'bond' is a 'unit of affinity,' it is something that can be 'satisfied,' when one bond of a carbon atom is satisfied by one bond of another carbon atom the loss of energy by the system is measured (ac-

according to Thomsen) by about 15,000 gram-units of heat, but when three bonds of a carbon atom are satisfied by three bonds of another carbon atom the loss of energy by the system is equal to zero.

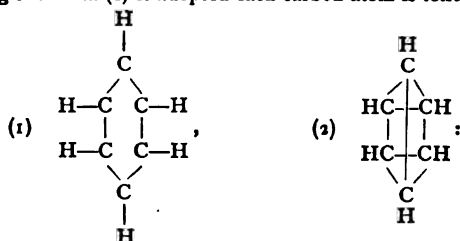
85. But if we regard Thomsen's results as teaching, in a general way, that the change from a material system of isolated atoms—say  $x$  carbon atoms,  $x'$  hydrogen atoms, and  $x''$  oxygen atoms—to a molecular system in which these atoms are combined so that all the carbon atoms are tetravalent (i.e. each acts on and is acted on by four other atoms) and all the oxygen atoms are divalent, is attended with the loss of a quantity of energy different from that which accompanies the change from the same system of isolated atoms to a molecular system in which some—say  $(x-2)$ —carbon atoms are trivalent, and some—say  $(x-1)$ —oxygen atoms are monovalent; if we regard this, or something like this, as the general lesson taught by Thomsen's results, then I think these results must be regarded as marking an advance in the conception of molecular structure.

86. But few measurements have yet been made of quantities of heat absorbed or evolved during similar chemical changes undergone by isomeric compounds, but those which have been made—e.g. heats of oxidation of benzene and its isomeride dipropargyl—seem to shew that in many cases at any rate the quantity of energy associated with one isomeride is different from that associated with another. Thus, the heat evolved during the complete combustion of dipropargyl ( $C_6H_6$ ) is about 850,000 gram-units, while that evolved during the combustion of the isomeric molecule benzene is about 800,000 gram-units; hence the amount of energy associated with the arrangement of six atoms of carbon and six atoms of hydrogen in the molecule of benzene is less, by about 50,000 thermal gram-units, than that associated with the arrangement of the same numbers of the same atoms in the molecule of dipropargyl. But in the molecule of benzene each carbon atom is at least trivalent (and possibly tetravalent), while in that of dipropargyl some of the carbon

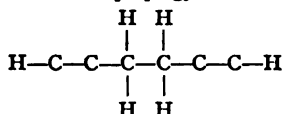
atoms are certainly divalent<sup>1</sup>; hence, it might apparently be concluded, that more energy is lost in the formation, from atoms of carbon and hydrogen, of a molecule in which all the carbon atoms act as tri- or tetravalent atoms, than of an isomeric molecule in which some of the carbons act as divalent atoms. But it must be remembered that in the benzene molecule each carbon atom acts on, and is acted on by, not more than one atom of hydrogen, and on at least two other atoms of carbon, whereas in the molecule of dipropargyl it is very probable that two of the carbon atoms act each on a single other carbon atom, and also that some of the atoms of carbon act each on two atoms of hydrogen. Hence, if we may provisionally draw a general conclusion from the limited data before us, it might be inferred that the differences between the quantities of energy associated with different atomic systems depend, among other conditions, on

- (1) whether each atom acts on, and is acted on by, the maximum number of other atoms which can come within its binding-sphere; in other words, on the actual valencies of the atoms in the molecules; and
- (2) on the nature of the atoms between which direct mutual action occurs.

<sup>1</sup> If Kekulé's formula (1) for benzene is adopted each carbon atom is trivalent; if Ladenburg's formula (2) is adopted each carbon atom is tetravalent;



the usually adopted formula for the dipropargyl molecule is



which contains 2 tetra- and 4 divalent carbon atoms.

87. The following data, in addition to the numbers given for the heats of combustion of benzene and dipropargyl, serve to illustrate the existence of a relation between the quantities of energy in molecules and the valencies of the atoms which form these molecules.

Empirical formula		Heat of combustion.	
$C_3H_6O$	(1) propaldehyde,	$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{C}-\text{C}-\text{C} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{H} \end{array} \\   \\ \text{H} \end{array}$	420,000 gram-units+.
	(2) allyl alcohol,	$\begin{array}{c} \text{H}_2 \\    \\ \text{H}_2=\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\   \\ \text{H} \end{array}$	442,000 gram-units+.

Assuming the correctness of these structural formulæ, it is seen that the propaldehyde molecule contains two tetra- and one trivalent carbon atoms, and also one monovalent oxygen atom, whereas the molecule of allylic alcohol contains two tri- and one tetravalent carbon atoms, and also one divalent oxygen atom.

88. The data of thermal chemistry furnish more numerous examples of the existence of a connection between greater or less molecular energy and the distribution of the mutual atomic actions within isomeric molecules.

Thus,

Empirical formula		Heat of combustion.	
$C_3H_4O_2$	(1) ethyl formate,	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{O}-\text{C}-\text{C}\equiv\text{H}_2 \\   \quad   \\ \text{O} \quad \text{H} \end{array}$	390,000 gram-units+.
	(2) methyl acetate,	$\begin{array}{c} \text{H}_2\equiv\text{C}-\text{C}-\text{O}-\text{C}\equiv\text{H}_2 \\   \\ \text{O} \end{array}$	395,000 gram-units+.

If the structural formulæ given are correct, then in each of these molecules we have two tetra- and one trivalent carbon atoms, and one mono- and one divalent oxygen atoms; but the trivalent carbon atom in ethyl formate acts

directly on two oxygen and one hydrogen atoms, and in methyl acetate on two oxygen and one carbon atoms: inspection of the formulæ will disclose other differences in the distribution of the atomic interactions.

Alcohol and methylic oxide afford another example of the relation we are discussing ;

		Heat of combustion.
Empirical formula $C_2H_6O$	(1) alcohol, $H_3 \equiv C - \overset{\overset{H}{ }}{\underset{\underset{H}{ }}{C}} - O - H$	330,000 gram-units +.
	(2) methylic oxide, $H_3 \equiv C - O - C \equiv H_3$	344,000 gram-units +.

We have here two molecules each containing a pair of tetra-valent carbon atoms, one divalent oxygen, and six monovalent hydrogen atoms, but in one of the molecules each carbon atom acts on three hydrogen and one oxygen atoms, while in the other the arrangement of atomic interactions is less symmetrical.

Another example is afforded by the three hydroxybenzoic acids ;

		Heat of combustion.
Empirical formula $C_7H_6O_3$	(1) 1 : 4 hydroxybenzoic acid, $C_6H_4(OH)CO_2H$	752,000 gram-units +.
	(2) 1 : 3 " " "	754,000 " " +.
	(3) 1 : 2 " " "	759,000 " " +.

89. The data are not sufficient to warrant any precise statement as to the relations between quantities of energy and molecular structure. It is possible that the case of benzene and dipropargyl is typical, and that of two isomeric molecules, one of which belongs to the class of ring-formed and the other to that of open-chain molecules, the former always contains relatively less energy than the latter. It is also possible that of two isomeric carbon compounds, the molecules of which belong to the open-chain class, and in which  $n_1 < 2n_2 + \dots 2$ , that containing the greater number of

tetravalent carbon atoms contains the smaller quantity of energy, provided that the distribution of the atomic interactions is the same, or nearly the same, in the two molecules. Or again it may be that when the actual valencies of the atoms in two or more isomeric molecules are the same, that molecule in which the atomic interactions are distributed so as to produce the greatest degree of symmetry is marked by the smallest amount of energy<sup>1</sup>. But we have as yet no accurate knowledge which may enable us to test the applicability of these suggestions.

Even if it could be asserted (as seems possible in a few cases) that this isomeride contains relatively less energy than that, and is therefore more stable, the question would arise, what do we mean by stability? For although of two molecules, *a* may be the more stable, as stability is measured by thermal changes, it may nevertheless be impossible to say that *a* is possessed of greater *chemical stability* than *b*. But a discussion of the meaning and application of the expression *chemical stability*, requiring as it does a knowledge of the facts and theories of chemical affinity, will find a fitter place in that part of this book which deals with chemical kinetics.

Inasmuch as variations in the physical properties of material systems accompany variations in the energies of these systems, it follows (if the two very general assumptions made on p. 176 concerning the connection between energy and structure of isomeric molecules are granted) that physical phenomena, other than thermal, may be expected to exhibit variations in isomeric molecules.

An attempt will be made in a future chapter to summarise the more important physical phenomena, between which and molecular structure in general there is an established connection. Here I would only remark that the researches of various chemists on the 'specific volumes' of liquid compounds, seem to shew, that the influence of any atom on the 'specific volume' of a compound molecule is dependent, not

<sup>1</sup> This view is put forward tentatively by Carnelley, *Phil. Mag.* [5] 13. 180. [In this paper will be found most of the thermal data bearing on the subject of the stability of isomeric molecules.]

only on the nature and on the actual valency of that atom, but also on the nature of the other atom, or atoms, between which and the given atom there is direct action and reaction. On the other hand, the work of Brühl has rendered it probable, that, in isomeric carbon compounds, the influence exerted by a polyvalent atom on the 'molecular refraction' is to a large extent dependent on the actual valency of that atom, i.e. on the number, rather than on the nature, of other atoms on which it acts directly<sup>1</sup>.

90. Much is to be expected from researches into the phenomena which occupy the border-land between chemistry and physics. If the knowledge chemists already have of the structure of molecules, meagre though that knowledge be, can be supplemented by definite dynamical conceptions, obtainable in part by the methods of thermal chemistry, then we may hope that chemistry will enter on a new stage of advance as a branch of the science of matter and motion. It seems to me that a most important step will be made if the bond theory of valency is generally abandoned; with it will go all those quasi-dynamical expressions, the offspring of loose and slipshod ways of thinking, which have gathered round that strange anomaly, a 'unit of affinity,' employed as a variable standard for measuring nothing.

If it be decided that by the valency of an atom is meant the maximum number of other atoms between which and the given atom there is, so far as we know, direct action and reaction in any molecule, then we are put in possession of a definite conception which may be applied to actually occurring phenomena, and the application of which will gradually lead to more precise knowledge regarding the distribution of the atomic interactions in various molecules. But at the same time that we are classifying molecules in accordance with the valencies of their constituent atoms and the distribution of the mutual actions of these atoms, in a word, in accordance with their structure, we are also becoming more impressed with the inadequacy of this classification; we see a vast field

<sup>1</sup> See *post*, chap. IV. par. 139.

opening for investigation, we see that measurements of losses or gains of energy are required, and that determinations of many physical constants are called for. We begin, I think, to perceive that this knowledge, when gained, will supplement and not supplant that which is already possessed by us, and that it will do this by leading to an exact knowledge of the way in which the variations in the energies of molecules are connected with changes in the configuration and motion of the atoms which constitute these molecules.

91. Admitting that the definition of valency given by Lossen furnishes a better working hypothesis than any other, it becomes necessary to inquire whether this definition and the conceptions which arise from it can be applied to all known cases of isomerism.

In the article ISOMERISM, by Dr Armstrong, in Watts's Dictionary, suppl. III., will be found an account of most of those compounds which are regarded as presenting phenomena inexplicable in terms of the usually adopted theory of isomerism.

If the facts in this article are classified, it will, I think, be apparent (1) that structural formulæ in keeping with reactions may be assigned to some of the isomeric compounds mentioned—e.g. to the acrylic acids, to maleic and fumaric acid, and to the acids obtained by heating citric acid—provided we cease to regard the conventional method of expressing valency by one or more straight lines, as affording any quantitative measurements, even relative measurements, of atomic interactions; (2) that other cases of unexplained isomerism—e.g. the dinitrochlorobenzenes, the nitrotetrabromobenzenes, and probably many of the terpenes<sup>1</sup>—are almost certainly illustrations of modifications in properties being correlated with variations in mutual actions between groups of molecules rather than between the atoms constituting each molecule; and (3) that the remaining cases are true residual phenomena,

<sup>1</sup> That optical properties are not always dependent on the structure of the molecule is shewn by the ease with which optically active amylic alcohol and valeric acid are converted into the inactive alcohol, and acid, without change of chemical properties. See Armstrong and Groves, *loc. cit.* p. 449.



at present inexplicable in terms of the prevailing theory but not therefore contradictory of that theory.

The theory of valency can only be applied to the molecules of gases: if this is remembered the so-called exceptional cases of isomerism appear no longer exceptional, they are simply assertions of the fact that our theory is partial.

Among the more important apparently inexplicable phenomena of isomerism are those presented by the terpenes, hydrobenzoin, dulcitol, the lactic and the tartaric acids, and the acids obtained by Perkin from coumarin<sup>1</sup>.

Chemists are quite undecided as to the structural formula to be assigned to any molecule the composition of which is represented by the empirical formula  $C_{10}H_{18}$ ; there is no need to bring within the theory hypothetical molecules which perhaps have no existence. We do not certainly know the molecular weights of hydrobenzoin and isohydrobenzoin; but assuming the generally employed formulæ to be molecular, it seems necessary to suppose that the molecule of one of these compounds contains two OH groups in direct combination with the same atom of carbon: our actual knowledge of the connections between molecular structure and stability is not advanced sufficiently for us to deny the possibility, although we may assert the improbability, of such a formula<sup>2</sup>. We know too little of the reactions of mannitol and dulcitol to enable us to decide between the possible structural formulæ of these compounds. Lactic and sarcolactic acids are extremely unstable; even in aqueous solutions they readily undergo changes; intermolecular actions are probably frequently occurring in any mass of either of these compounds. Tartaric and lævotartaric acids may have different molecular weights; the differences in physical properties which they exhibit are differences between solids, and we know almost nothing of the laws regulating molecular phenomena in liquid and solid bodies. Perkin<sup>3</sup> has described two series

<sup>1</sup> See the article by Armstrong, *loc. cit.*

<sup>2</sup> It seems however very probable that these two compounds belong to the class of 'physically isomeric' bodies; see Zincke, *Annalen* 198. 191.

<sup>3</sup> *C. S. Journal. Trans. for 1881.* 409.

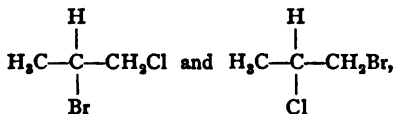
of acids derived from coumarin, having the same elementary composition but differing in physical properties; any one acid is generally changeable into its isomeride by the action of heat, the process being in many cases reversible by the same agency. But these changes are accompanied by processes of hydration and dehydration, and would appear to consist in great part of intermolecular actions, and not only in interactions of the atoms constituting the molecules. But of intermolecular actions we know as yet very little.

92. The properties of any mass of a solid or liquid compound seem to be conditioned, not only by the valencies of the atoms which constitute the molecule of that compound, by the distribution of the atomic actions within the molecule, and by the relatively large or small quantity of energy associated with this atomic configuration, but also by actions and reactions between groups of molecules, the parts of which groups hold together during more or less wide variations in the physical conditions to which the compound may be subjected<sup>1</sup>.

The hypothesis that groups of molecules, marked by fairly definite properties, may exist, and may mutually act and react, enables us to give a partial explanation of various facts concerning liquid and solid compounds which cannot, apparently, be so well explained by any other molecular hypothesis that has been suggested.

The phenomena presented by calcium carbonate are typical of those to be explained by the help of the hypothesis in question. Calcspars and arragonite are composed of calcium, carbon and oxygen united in the proportions expressed by the formula  $\text{CaCO}_3$ ; arragonite crystallises in rhombic forms,

<sup>1</sup> According to Henry [*Ber.* 4. 604], the two chlorobromopropanes,



are identical in physical properties: if this is really so, we have an instance of identity of physical properties accompanied by a slight difference in the distribution of atomic interactions within the molecule.

calcspars in hexagonal forms; arragonite is harder, and specifically heavier than calcspars, nor is it so easily acted on by various reagents, e.g. hydrochloric or acetic acid, or ammonium chloride or nitrate; when powdered arragonite is heated to redness it is changed into calcspars, but the reverse change is not accomplished by the same agency; both modifications of calcium carbonate can be produced at low temperatures, but there is a certain temperature above which only calcspars is formed. Calcspars and arragonite thus exhibit identity of elementary composition (perhaps the same molecular weight) accompanied by differences of physical, and to some extent of chemical properties. Another typical instance is afforded by antimonious iodide,  $\text{SbI}_3$ ; this compound crystallises in red-coloured hexagonal forms, which when heated to  $114^\circ$  are suddenly changed into a mass of yellow-coloured orthorhombic crystals, the original external form of the mass being however preserved<sup>1</sup>. Several carbon compounds (apparently all belonging to the class of benzenoid compounds) exist in more than one form, each modification being characterised by a definite melting point and generally also by a special crystalline form. Thus chlorodinitrobenzene— $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$  [1 : 2 : 4]—is said to form monoclinic crystals which melt at  $36^\circ$ , and also rhombic crystals which melt at  $39^\circ$ . Anthracene,  $\text{C}_{14}\text{H}_{10}$ , crystallises in monoclinic plates melting at  $213^\circ$  which are easily oxidised by the action of nitric acid to anthraquinone ( $\text{C}_{14}\text{H}_8\text{O}_2$ ); when a solution, in benzene, of anthracene is exposed to sunlight small prismatic crystals separate, melting at  $244^\circ$ , having the composition  $\text{C}_{14}\text{H}_{10}$ , but not acted on by nitric acid, and not oxidised to anthraquinone by chromic acid<sup>2</sup>. A very remarkable instance of the phenomenon under consideration is presented by the derivative of diphenyl to which the formula  $(\text{C}_6\text{H}_5\text{BrNHCOC}_6\text{H}_5)_2$  is assigned. This compound melts at  $195^\circ$ ; if the melted substance is *cooled quickly* and again heated its melting point is now  $99^\circ$ ; but if heating is continued the liquid again solidifies at  $125\text{--}130^\circ$ , and the solid thus obtained melts once more at  $195^\circ$ . Finally

<sup>1</sup> J. P. Cooke, *Proc. Amer. Acad. of Arts and Sci.* [2] 8. 72.

<sup>2</sup> See Armstrong and Groves, *loc. cit.* p. 199.

if the solid which melts at  $195^{\circ}$  is raised to that temperature and then *slowly cooled*, the product possesses the normal melting point, viz.  $195^{\circ}$ . When a substance crystallises in more than one system, one crystalline form approaches as nearly as possible to the other, one form appears to imitate the other both crystallographically and optically<sup>1</sup>; thus arsenious oxide crystallises in regular octahedra and also in rhombic prisms, the latter exhibiting an angle identical with the angle of the regular octahedron.

93. O. Lehmann<sup>2</sup> has collected and discussed many instances of the exhibition of different physical properties by compounds possessing the same elementary composition<sup>3</sup>. The phenomenon, which may be called *physical isomerism*<sup>4</sup>, presents analogies with allotropy (see *ante*, par. 67); in both, temperature is the most important condition affecting the change from one form to another, and this change is accompanied in both classes of phenomena by absorption or evolution of heat.

In the term allotropy are summed up similar phenomena which appear to be best explained, in terms of the molecular theory, by the hypothesis that variations in the numbers of atoms, all of one kind, constituting a molecule, may be accompanied by variations in the physical, and to some extent chemical properties, of the substance which is composed of these molecules. But the term is also applied to phenomena—e.g. the variation in melting points, &c. of solid sulphur—which are probably better explained by the hypothesis that what may be called the acting physical unit, or the *physical molecule*, of each allotropic form is constituted of a different number of chemical molecules. In this view of the matter,

<sup>1</sup> See E. Lehmann, *Ber.* 15. 2835.

<sup>2</sup> Pasteur, *Ann. Chim. Phys.* [3] 23. 267.

<sup>3</sup> *Zeitschr. für Krystallog.* 1. 97. See also, in connection with the subject generally, the article 'Isomerie, physikalische' in *Neues Handwörterbuch der Chemie*, Bd. III. pp. 836—843.

<sup>4</sup> On this subject see also Laubenheimer, *Ber.* 9. 760.

<sup>5</sup> The term physical isomerism seems to have been first used by L. Carius, *Annalen*, 126. 214 (see also *do.* 130. 237).

the term physical isomerism would embrace phenomena common to elements and compounds.

94. Lehmann (*loc. cit.*) divides physically isomeric bodies into two classes: (1) those in which change from one form to another occurs at a definite temperature, the direction of the change being dependent on very small differences of temperature; (2) those which exhibit two forms, one more stable than the other, and in which change from one form to the other does not occur at a definite temperature, and is not reversible by heat alone.

Ammonium nitrate is an example of a substance belonging to the first class; the rhombic crystals of this salt, which separate at ordinary temperatures from an aqueous solution, melt at (about)  $168^{\circ}$ ; as the molten mass cools crystals belonging to the regular system are formed, but at (about)  $125^{\circ}$  these change to rhombohedral forms, which at (about)  $87^{\circ}$  are converted into rhombic needles, from which, at  $30^{\circ}$  or so, the original rhombic crystals are produced. If the rhombic crystals are again slowly heated, the rhombic needle-shaped crystals form at (about)  $30^{\circ}$ ; the rhombohedral forms appear at (about)  $87^{\circ}$ , the regular crystals at (about)  $125^{\circ}$ , and finally the solid melts at  $198^{\circ}$ . Again, if a little sulphur is melted on a microscopic slide (under a cover), and the slide is arranged so that temperature can be easily regulated<sup>1</sup>, monoclinic crystals are produced, but, as temperature falls, these change into rhombic forms, and it is possible to regulate the temperature so that definite amounts of each form exist simultaneously, but on the slightest change of temperature the rhombic crystals grow at the expense of the monoclinic, or *vice versa*.

The behaviour of dibromopropionic acid when heated illustrates the nature of the changes which characterise substances belonging to Lehmann's second class of physical isomerides. This substance crystallises in rhombic forms which melt at  $64^{\circ}$  (about); if the molten mass is heated a few degrees above this point rhombic crystals ( $M.P = 64^{\circ}$ )

<sup>1</sup> Lehmann describes an apparatus for this purpose (*loc. cit.* pp. 102—3).

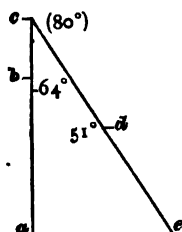
are again produced on cooling; but if the molten substance is heated many degrees above  $64^{\circ}$  and is then allowed to cool, small flat nearly right-angled tables are obtained which melt at  $51^{\circ}$  (about). If the less stable form (M.P. =  $51^{\circ}$ ) is slowly heated under the microscope, growth of the other (more stable) crystals is noticed; the growth at first is rapid, then slower, but before the change has gone far the melting point of the less stable crystals is reached and the whole mass becomes liquid. If the more stable form is melted, heated some degrees above  $64^{\circ}$  and then brought into contact with crystals of both forms, growth of each modification proceeds until the crystals touch, after which the more stable (higher melting) crystals grow into the others until the latter are completely changed into the stabler forms. Another instance is furnished by paranitrophenol. This compound crystallises from hot aqueous solutions in monoclinic crystals, and from cold aqueous (or alcoholic) solutions in crystals belonging to the same system but differing in form and melting point from the others. By fusing either form and allowing the molten mass to cool, only the less stable (lower melting) crystals are produced; but if a little of the substance is melted on a microscopic slide, and a crystal of the second (stabler) form is placed in contact with the edge of the solidified mass, and heating is then again commenced, crystals of the stabler form begin to grow at the expense of the other crystals, at first rapidly, then more slowly, until both forms melt, the less stable at a lower temperature than the more stable.

95. I do not think that a rigid classification of physical isomerides into two groups can be carried out. The examples given shew that there are certain broad differences between the two classes; but a detailed consideration of these examples, and of others to be found in Lehmann's paper, seems to me to lead to the conclusion that there exists no firmly drawn line of separation between the phenomena exhibited by substances placed in different classes. This will, I think, be more apparent if some of the facts enumerated are represented in a roughly graphic manner. Let us compare the

action of heat on ammonium nitrate, dibromopropionic acid, and paranitrophenol.

Let that form of ammonium nitrate which crystallises in regular crystals be called *A*, that which crystallises in rhombohedral forms *B*, that in rhombic needles *C*, and that in ordinary rhombic forms *D*. Let the line *ab* represent the interval of temperature through which ordinary ammonium nitrate must be heated until it melts; now let the molten substance cool, that part of the line *ab* between  $168^{\circ}$  and  $125^{\circ}$  represents the temperature-interval through which the salt exists in form *A*, that part between  $125^{\circ}$  and  $87^{\circ}$  represents the temperature-interval through which form *B* is stable, that part between  $87^{\circ}$  and  $36^{\circ}$  the interval through which form *C* is stable, and lastly the portion below  $36^{\circ}$  represents the interval of stability for form *D*. The operation represented by the line *ab* is reversible; whether we begin at *a* or *b*, the salt goes through the several stages roughly indicated in the diagram.

Now turn to dibromopropionic acid. Let the rhombic form melting at  $64^{\circ}$  be called *A*, and the small tables melting at  $51^{\circ}$  be called *B*. The line *ab* represents the temperature-interval through which *A* is stable; on heating *A* to  $64^{\circ}$  it melts, but on cooling, it so to speak runs back along the same line: now let *A* be raised from *a* to *c*, say  $16^{\circ}$  above its melting point, and then allowed to cool; a new substance, *B*, has been produced, and this substance is stable throughout the interval *ce* (between *d* and *e* it is solid, between *c* and *d* it is liquid). Although *B* cannot be changed into *A* by heat alone, yet when *B* is somewhere between *c* and *d* (i.e. when it is molten) it may be partially converted into *A* by contact with small portions of *A*. If the symbols *A* and *B* are used to represent the two forms of paranitrophenol, then *B* may be almost wholly converted into *A* by contact with *A*. Because of its lower melting point, *B* has been called the less stable form of dibromopropionic acid,



but if we consider that it cannot be changed into *A* by the action of heat we should say that, thermally looked at, *B* is the more stable form of this substance.

If we now treat the facts concerning the diphenyl derivative mentioned on p. 184, par. 92, diagrammatically we shall have this result: (let the form melting at  $195^{\circ} = A$ , and that melting at  $99^{\circ} = B$ ). The line *ab* represents the temperature-interval through which *A* must be raised in order to melt it: let the molten substance cool slowly, it runs back along the same line *ab*; [? do any crystallographic changes occur along this line]; but let *A* cool quickly, it seems to get, so to speak, shunted off the line of normal stability on to the line *bd*: *cd* represents the interval through which it exists in solid form and *ce* the interval (roughly) through which it is stable in liquid form, for when *B* has again been heated to  $125^{\circ}$ — $130^{\circ}$  it solidifies, and is found to have come back to form *A*, i.e. to the line of normal stability<sup>1</sup> (*ab*).

This diphenyl derivative appears to belong to both of Lehmann's classes: some of the changes which it undergoes are to a great extent reversible and occur at definite temperatures, others are not reversible and occur gradually throughout a considerable interval of temperature.

Substances of which ammonium nitrate is the type appear to be less profoundly modified by the action of heat than substances belonging to the class represented by dibromopropionic acid. Substances belonging to the first of these classes shew analogies with the so-called molecular compounds (e.g. compare the action of heat on crystallised sodium phosphate, or on hydrated cobalt salts<sup>2</sup>, with that on dibromopropionic acid or on paranitrophenol); and the course of the change brought about by the action of heat on these bodies shews

<sup>1</sup> It seems probable that if *A* were heated to  $195^{\circ}$  and cooled quickly to  $130^{\circ}$ , and then *very rapidly*, it would solidify at that point, and afterwards be found to melt at  $195^{\circ}$ .

<sup>2</sup> See *post*, section 5, par. 102.



some analogies with the processes of gaseous dissociation<sup>1</sup>. For these reasons Lehmann has summarised the phenomena characteristic of bodies of this class under the term *physical polymerism*, and the phenomena characteristic of bodies of the other class under the term *physical metamerism*. The former term implies that the physically different forms exhibited by a substance belonging to this class are to be regarded as associated with the existence of physical molecules, each formed by the grouping together of a different number of chemical molecules (as defined in Chap. I. par. 13, p. 25). The term physical metamerism on the other hand implies that the physical molecule of each different form of a substance belonging to this class is composed of the same number of chemical molecules, but that the arrangement of these is different in each case.

Lehmann's classification is certainly based on no fanciful analogies. Polymerism and metamerism are well marked phenomena among gaseous molecules; and the hypothesis of the existence of groups of molecules characterised by definite properties, but each of which groups is readily decomposed by heat; appears to be as simple as any other that can be proposed to explain the observed facts. Moreover this hypothesis is almost forced on our acceptance when we consider the numerous and varied phenomena summarised in the term 'molecular-compounds<sup>2</sup>.' But the analogy between the reactions of gaseous molecules and the changes undergone by solid and liquid substances may be pushed too far; we ought to recognise how small and inexact our knowledge is of the molecular actions of the latter classes of bodies. Qualification of the terms molecule, polymerism, and metamerism by the adjective physical widens the meanings of these terms by making them applicable to a larger class of phenomena, but at the same time it makes the application less precise<sup>3</sup>.

<sup>1</sup> See Book II. Chap. 11.

<sup>2</sup> See *post*, section 5.

<sup>3</sup> Lehmann considers in considerable detail the phenomena attending the change of one form of a substance into another; he divides the changes into groups, according as both forms are solid, or one solid and one liquid, &c. As the

96. We have thus found that to trace the connections between the composition and the properties of changing material systems has always been regarded as the fundamental problem of chemistry. Attention has sometimes been almost confined to the composition of substances forming such systems, at other times the properties of the system and its components have been regarded as chiefly important. We found that as chemistry advanced it became necessary to know more than the mere elementary composition of bodies; having gained the atom and the molecule, chemists were soon convinced that the arrangement of the same atoms might vary, and that

subject is important I give a brief resumé of some of Lehmann's results in this note, but the original paper ought to be studied by all who are interested in the subject.

- A. Change of one, more complex, solid form of isomeride to another, less complex, solid form, attended with absorption of heat; physical molecules of both kinds are present simultaneously, but at a certain temperature change will occur. If one modification is heated alone, the normal temperature of change may be largely exceeded without a complete change to the second modification, but at such a high temperature contact with the second modification may determine sudden and complete change.
- B. Change of solid form to liquid form, occurring with heat absorption at a definite temperature dependent on the pressure; the change will not be complete, as molecules of both kinds will exist together. If the specific gravity of the solid form is greater than that of the liquid form, then on heating past the melting point there will be rapid expansion as the physical molecules of the solid form are separated into those of the liquid; this will be followed by a slower regular expansion. If the specific gravity of the solid is less than that of the liquid, expansion will be small, or even negative, until a point of maximum density is reached, after which expansion will proceed at the normal rate.

In some cases a solid form is changed, by the action of heat, into a liquid form, which, at a higher temperature, is again changed into a second solid form, e.g. when selenion is heated till it becomes viscous and is kept at this temperature for some time it changes into a crystalline form. So in the change of yellow to red phosphorus by the action of heat; in this case the molecules which form the liquid phosphorus are kept apart for some time, by the energy added as heat acting against cohesion, and so are allowed to re-arrange themselves in loose groups.

- C. Change of liquid, to solid modification is complex: a few crystals form and determine the crystallisation of the whole mass; in some cases the liquid, especially if viscous, may be cooled below the temperature at which crystallisation normally begins, and may then pass into an amorphous solid form.

properties might therefore be correlated not only with atomic composition but also with atomic configuration. We traced this conception through the dualism of Berzelius and the unitary system of Dumas, Laurent, Gerhardt and others, through the hypothesis of compound radicles and that of types, to the time when Frankland and Kekulé gave it greater precision by arranging the elementary atoms in groups according to the maximum number of other atoms with which each was found to combine.

But we saw that the expression equivalency (or valency) of atoms gradually came to be used in a loose and inexact manner. We found that the comparison of monovalent with divalent, &c. atoms, when unchecked by accurate dynamical knowledge, led to the belief that the term in question expressed in some vague way quantitative measurements of interatomic forces, and to the conclusion that, inasmuch as one divalent atom could directly bind to itself two other atoms, while one monovalent atom could act directly on only a single other atom in a molecule, therefore the divalent atom was capable of exerting twice as much force as the monovalent atom. The latter part of the foregoing sentence may I think be taken as fairly representative of the loose and slipshod way in which dynamical language has too often been used in chemistry.

We found that attempts were made to build a general theory of valency on a shifting quasi-dynamical foundation; but the account given in this section of Lossen's criticisms of the expressions 'a bond,' 'a valency,' 'a unit of affinity,' &c. has I think been sufficient to shew how inexact, while apparently precise, and how narrow, while apparently far-reaching, the theory in question really is.

The objections raised against the atomic theory in recent years by some chemists, who nevertheless made free use of the essentially atomic conceptions of modern chemistry, led, it seems to me, to a looseness of thinking about atoms, molecules and equivalents, which has done no little harm. *Parts by weight* were spoken of as if the expression were synonymous with *atom*; *equivalents* were regarded as acting and

reacting one on the other; there appeared to be a possibility of chemistry retracing her steps to the time when no precise meaning was attached to any of the terms *atom*, *molecule*, *combining weight*, *equivalent*, but each was used as nearly synonymous with the others. From the possibility of such retrogression we have been saved by the general advance of physical science. As the molecular theory of matter became more precise and its applications more far-reaching, it was impossible for chemists to employ conceptions essentially molecular and atomic and at the same time to express chemical changes in a notation based on the notions of a pre-molecular era. It became necessary to choose definitely between the atom and the equivalent, and the great body of chemists has certainly chosen the former.

But as soon as attempts to found a theory of chemical actions on the basis of equivalents was abandoned, it was seen that the conception of equivalency might be retained and applied to the elementary atoms. To keep distinct the conceptions implied in the terms equivalent and atom, and at the same time to arrange the atoms in equivalent groups, is one of the problems of modern chemistry. On this distinction and on this resemblance is based the theory of isomerism. The study of isomerism has done much, we found, to render precise the conception of the molecule as a structure with properties dependent on the nature, the number, and the arrangement of the constituent atoms.

We endeavoured to subdivide the conception expressed in the words 'arrangement of atoms in a molecule' into parts, and to demonstrate by illustrations the existence of a connection between each of these parts and the properties of the molecule. These illustrations led to clearer notions concerning valency of atoms, and the meaning of structural formulæ; these formulæ we regarded as expressing the actual valencies of the atoms in the molecule,—i.e. the number of atoms directly acting on and acted on by each atom,—and as expressing also the distribution of the atomic interactions, i.e. the nature of the atoms in direct mutual connection; but we tried to attach no quantitative meaning to the symbols used

for expressing atomic valencies and distributions of atomic interactions.

The theory of valency, as thus used, leads to dynamical conceptions, but regards these as outside its sphere: it points the way along which progress will be made. Attempts must be made to apply thermal, optical, and other physical methods of research to the investigation of chemical problems; thus we may hope to gain clear and precise knowledge regarding the connection between structure and stability of molecules, in so far as the latter is measured by variations in the quantities of energy associated with each molecule.

#### APPENDIX TO SECTION IV.

97. To have given a detailed account of Lossen's criticisms of the generally accepted views regarding 'valencies' or 'units of affinity' in the text of the section on isomerism, would have involved too great an interruption of the main argument of that section. But as Lossen's criticisms seem to me of great importance I propose to give some account of them here.

The many and varied hypotheses concerning valency set forth by chemists of acknowledged authority may be divided, says Lossen, into three groups:—

I. Those hypotheses which regard 'an affinity' as a definite quantity of matter, or as an action of some kind proceeding from a definite quantity of matter.

II. Those which regard 'an affinity' as a part of an atom, or at least as something connected with a part of an atom.

III. Those which regard the 'affinities' of an atom as definite forms of motion of the atom.

I. Erlenmeyer<sup>1</sup> has developed the conception of 'Affinities' or 'valencies.' He states, as a rule without exceptions, that 'in all chemical combinations a constant quantity of one element

<sup>1</sup> For references to the work of the various chemists mentioned, see Lossen, *loc. cit.*

'always attracts a constant quantity of another.' These constant quantities are the 'affinivalencies' of the elements: one affinivalency of element *a* always binds to itself one affinivalency of element *b*. The affinivalency of carbon = 3, of oxygen = 8. In  $\text{CO}_2$  we have 3 parts by weight of carbon combined with 8 of oxygen, but in CO the same amount of carbon with only 4 parts by weight of oxygen; Erlenmeyer's general law is therefore erroneous. If it be said that a constant quantity of one element *attracts* (not combines with) a constant quantity of another, then, as in  $\text{CO}_2$  6 parts by weight of carbon attract 16 of oxygen, we must suppose that in CO 16 parts by weight of oxygen are attracted by 6 of carbon, and that the remaining 6 of carbon have no attractive action on the oxygen.

Atoms and relative quantities of matter are compared by Erlenmeyer, but *relative* quantities do not attract each other. In the molecule CO there is one atom of carbon and one atom of oxygen, and these atoms attract one another; half an atom cannot attract because it has no existence. The hypothesis that an atom is nonhomogeneous, although indivisible, might be made, but is not made, by Erlenmeyer. If an equivalent is regarded as a constant quantity, this quantity attracts sometimes one, sometimes two (or more) equivalents of other elements. The molecule  $\text{CH}_4$  contains one atom of carbon and four atoms of hydrogen; we may say that 3 parts by weight of carbon here attract 1 part by weight of hydrogen: so in  $\text{CCl}_4$  it may be said that 3 parts of carbon attract 35.5 parts of chlorine. But in  $\text{CH}_3\text{Cl}$  12 parts of carbon attract 3 parts of hydrogen *and* 35.5 parts of chlorine; in place of 12 parts of carbon we may, if we choose, say 9 + 3 parts, just as we might say that  $7 + 5 = 12$ , or  $\sqrt{144} = 12$ ; but we cannot say that 9 parts of carbon attract 3 parts of hydrogen and the remaining 3 parts of carbon attract the 35.5 parts of chlorine. If we suppose the carbon atom to be perfectly homogeneous, then the whole atom acts on the chlorine atoms and on each of the hydrogen atoms: if we suppose that the atom of carbon is possessed of a structure, it remains to explain in what respect one part of the atom differs from other parts;

but *a part of an atom* is not the same thing as *a fraction of the relative weight of an atom*.

Hofmann speaks of 'an affinity' as a force proceeding from a constant mass of an element, which mass he regards as the equivalent, and defines it as 'the minimum atom-binding quantity' of the element. He nevertheless uses equivalent as a varying quantity. By an arbitrary choice of certain values for the equivalents of the elements it is possible that the number obtained by dividing the atomic weight by the equivalent weight of any element should be the same as the number expressing the maximum number of hydrogen atoms which can be bound by one atom of the given element.

L. Meyer also speaks of the action of quantities by weight of one element on atoms of another element. In one place he defines equivalent quantities of elements as those quantities which are able to bind to themselves, directly and without the intervention of a third substance, equal quantities of other substances. We should expect 16 parts by weight of oxygen to be equivalent to 12 parts by weight of carbon, and to 14 parts by weight of nitrogen, because 16 parts of oxygen directly bind 16 of oxygen in  $O_2$ , 14 of nitrogen in  $NO$ , and 12 of carbon in  $CO$ : but L. Meyer supposes two free affinities in the last named molecule, i.e. he supposes that  $\frac{1}{2}$  carbon bind 16 of oxygen, although the molecule  $CO$  contains one indivisible atom of carbon and one indivisible atom of oxygen.

Those hypotheses in which 'affinities' are regarded as constant weights of matter, or as actions proceeding from constant weights, arise, according to Lossen, from not sufficiently marking the distinction between equivalent and atom. Equivalent, or combining, weights are relative weights of divisible masses; atomic weights are relative weights of indivisible masses. If the atomic hypothesis is adopted, we must regard atomic weights as relative weights of mutually reacting bodies; but equivalent weights, in so far as they differ from atomic weights, are relative weights of imagined sums, or fractions, of these bodies. Bodies, whose relative weights are equal to these equivalent weights, do not mutually react within molecules. To find equivalents, parts by weight

should be compared with parts by weight, or atoms with atoms.

II. Besides the hypothesis of 'affinivalencies' already referred to, Erlenmeyer also speaks of mutual actions between atoms as occurring at certain points of these atoms. This may mean either that contact (not of course absolute contact) between the reacting atoms is made at these points, or that mutual atomic action occurs only when these attracting points coincide. The attracting points must be considered as qualitatively different from the rest of the atoms. The form of polyvalent atoms must be such that several points of one can touch the same number of points of another: the positions of the points must be such that when some of these points are in contact it is not necessary that all should be in contact. To fulfil these conditions without supposing the form of the atoms, or at any rate the positions of the points, changeable, is exceedingly difficult. This hypothesis of Erlenmeyer tends to foster the notion of an attractive force proceeding from different points of elementary atoms; Kekulé's graphic formulæ do not, probably, imply this conception, but these formulæ may be, and have been, used as if this conception were true.

A qualitative difference between parts of an atom, can only mean that some parts are chemically active while others are chemically inactive. If the inactive parts are composed of imponderable matter then each  $n$ -valent atom must be made up of  $n$  atoms; we thus arrive at atomic weights different from those on which the science of chemistry at present rests. If the inactive parts consist of ponderable matter, then in the case of action between different atoms we have action through the ether, but in the case of action between parts of the same atom we have action through ponderable chemically inactive matter. In either case it appears that the notion of atom must be very different from that at present adopted, and, it would seem, necessarily adopted, if facts are to be explained.

But it may be supposed that the active parts of the atom are in a different electrical condition from the inactive parts. If electricity be a form of motion, then some parts of an indi-



visible atom must be supposed in motion while others are not; if electricity be a fluid, then we have a material difference, arising from the partial fixation of this fluid, between the active and inactive parts of the atom. Both of these hypotheses are opposed to the fundamental conception of atom<sup>1</sup>.

Michaelis has supposed that the attractive force of an atom is exerted in certain fixed directions only. On this hypothesis a straight line joining two atoms which are directly bound together may be regarded as expressing the direction of the mutually exerted force; an  $n$ -valent atom has  $n$  such directions. If this atom is directly bound to fewer than  $n$  atoms, say to  $n-x$  atoms, then the mutual action is exerted in  $n-x$  directions. Lossen expresses his general agreement with this interpretation of the hypothesis of Michaelis. But if that chemist supposes that to every atom, regarded as a point, there are *always* attached a fixed number of such 'lines of force,' then it is asked 'on what does the atom act when it is bound to less than its maximum number of other atoms?'

The objection urged to van't Hoff's form of the hypothesis now being discussed, is, that by this chemist the 'affinities' of an atom are imagined as arranged in a definite form in space; but as we cannot define an 'affinity,' much less can we assign geometrical figures to the arrangement of these 'affinities.'

III. L. Meyer supposes that there is one position at which a monovalent atom during its vibration can combine with another atom to form a stable compound, that there are two positions at which a divalent can combine with another atom, and so on. In the molecule  $\text{NH}_3$ , we have one trivalent and three monovalent atoms; the nitrogen atom swings through three positions, at each of which it can take up one hydrogen atom. In the molecule  $\text{OH}_2$ , the divalent oxygen

<sup>1</sup> This criticism is rather weak: we know too little as to what electricity is to hazard such criticism as this; besides, Helmholtz has shewn that there is probably a close and definite connection between the valency of an atom and the electrical charges on that atom; see book II.

atom swings through two such positions. In the molecule NO it appears as if the three positions of possible combination passed through by the triad nitrogen atom must be also touched by the path of the diad oxygen atom, but if so the oxygen atom may, in some circumstances, be trivalent.

The results of O. E. Meyer's physical and dynamical investigation of the forms of molecules are not in harmony with this view of L. Meyer. The form of a molecule would appear to be dependent more on the number of the constituent atoms than on the valencies of these atoms. But on L. Meyer's hypothesis the nature of the path of the atoms swinging in the molecule must condition the form of the molecule, and the nature of this path is itself conditioned by the valencies of the atoms.

Kekulé has advanced hypotheses as to the motion of atoms within molecules, but these hypotheses are not sufficiently definite to admit of detailed criticism. Lossen however objects to applying to the motion of atoms within molecules the conceptions which arise from a study of the motion of molecules in a confining vessel. If the atoms composing a mass of hydrogen molecules undergo mutual collisions, why, when they have separated a certain distance from one another, is the direction of their motion changed until a second collision occurs? There is no confining molecular wall answering to the sides of a containing vessel. If it be supposed that the atoms in molecule *a* enter into collision with the atoms in molecule *b* or *c*, then this is equivalent to asserting that a mass of hydrogen is composed not of diatomic, but of monatomic molecules<sup>1</sup>.

98. Among the various developments of the bond-theory of valency not mentioned in the text, is that which concerns itself with the question whether all the bonds of a polyvalent atom are of equal value, or whether one may be 'stronger' than another. If the criticism applied to the subject of

<sup>1</sup> Here again, I think Lossen carries his criticism too far. The methods of molecular enquiry are necessarily statistical; a mass of hydrogen may contain many free atoms (or monatomic molecules), and yet for all practical purposes behave as if composed entirely of diatomic molecules.

bonds generally is just, it follows, I think, that the question alluded to is meaningless; but as it has been hotly disputed about, it may be well briefly to consider it here.

It is assumed in the bond-hypothesis that the so-called affinities of atoms attract or satisfy one another, and hence those affinities of one atom which are not satisfied by affinities of another, must be satisfied by other affinities of the atom itself. No molecule, it is sometimes said, can contain an odd number of atoms of uneven valency. This outcome<sup>1</sup> of Gerhardt's 'law of even numbers' (see *ante*, chap. I, par. 36) is however contradicted by the existence of the molecules I, NO, NO<sub>2</sub>, ClO<sub>2</sub>, WCl<sub>6</sub>, VCl<sub>4</sub> or VOCl<sub>3</sub>, and cannot therefore be accepted as a statement of facts, unless indeed the valency of an atom is a number susceptible of arbitrary variation. That the maximum valency of each atom is fixed is generally admitted. One school however holds that (e.g.) a tetrad atom is always tetrad, another school that a tetrad may function as a diad atom; in the molecule CO, for instance, the carbon atom, it is said, is tetrad, but two of its affinities are mutually satisfied. The opponents of this view would say that in CO the carbon atom is divalent, the other pair of bonds being latent. The dispute has been wholly a battle about words. Whether the bonds are latent, or are mutually satisfied, they are equally existent: as Lossen remarks, '*zwei und zwei geben doch immer vier.*'

But if always existent, are the bonds always of equal value? Are the two pairs of bonds which hold the two oxygen atoms to the carbon in CO<sub>2</sub> equal in value to twice the pair of bonds by which one oxygen atom is held to a carbon atom in the molecule CO?

Now if we wish to compare things we must have a standard; but I think sufficient facts have been enumerated to shew that no standard exists in terms of which the expression 'value of a bond' may be stated. Even if the valency of an atom is regarded as expressing the total number of parts into which the chemical energy of that atom is divisible, this

<sup>1</sup> The statement is sometimes put in this form; "the sum of the valencies, or affinities, of the atoms in any molecule is always an even number."

must mean, that the energy is divisible when there is mutual action between the given atom and other atoms in a molecule. Thus; assume for a moment that the chemical energy of an atom of carbon is divisible into four parts, it does not follow that each part represents a fourth of the whole energy or always represents the same portion of that energy. To take an illustration, in the stable molecule CO we must suppose, on this hypothesis, that the whole of the chemical energy of the carbon atom is employed in the transaction symbolised by the formula  $C-O$ ; again, in  $O-C-S$  the whole of the energy of the carbon atom is employed, but the energy represented by  $O-C$  is probably different from that represented by  $C-S$ , and the sum of these is probably different from that represented by the expression  $O-C-O$ . The number of possible ways in which the energy is distributed is, on this hypothesis, measured by the valency of the atom, the amount of the energy employed in any atomic transaction depends on the nature of the atom or atoms between which and the given atom there is mutual intramolecular action<sup>1</sup>.

Even if we adopt this, the most dynamical view of valency that can be adopted with any safety, the controversy concerning equal and unequal bonds is seen to be a mere logomachy<sup>2</sup>.

<sup>1</sup> For a fuller working out of this way of regarding valency see Claus, *Ber.* 14. 432.

<sup>2</sup> It is sometimes said that the hydrogen atoms in the molecule of benzene are of equal value, but when one of these atoms is replaced by a radicle, the remaining five are of different values relatively to the radicle introduced into the molecule. To make such a statement as this, it seems to me, is to employ the term value in too loose and vague a way. All the hydrogen atoms in a molecule of a mono-derivative of benzene are monovalent, and therefore of equal value so far as 'proportion in exchange' for chlorine, bromine &c. goes. What appears to be meant by the statement in question is, that more than one mono-derivative (chloro- bromo-.....or generally  $X$ -derivative) can be obtained from the molecule  $C_6H_5X$ ; but this is simply a special illustration of the general proposition that the properties of compounds are not wholly dependent on the valencies of their constituent atoms.

SECTION V. *Molecular Compounds.*

99. The adjectives molecular and atomic have been employed by Kekulé<sup>1</sup> and others to distinguish those compounds which separate into two or more other substances when heated, from those which can be vaporised without decomposition. Ammonium chloride, which when heated yields a vapour containing ammonia and hydrochloric acid, may be taken as a typical molecular compound, and water, the vapour of which contains only molecules of water-gas, as a typical atomic compound.

This division of compounds has played an important part in the development of the theory of valency. Kekulé has always insisted that facts regarding atomic compounds can alone be employed as data for finding the valencies of elementary atoms; his opponents have retorted by demanding a definition of molecular as opposed to atomic compounds, and by shewing that every proposed definition fails when applied to actual phenomena.

But it is not so much as concerns the theory of valency that the distinction implied in the words atomic and molecular compounds ought, I think, to be insisted on; if the arguments put forward in the preceding section are of any value, we must agree to confine the theory of valency, at present, to gaseous compounds. There are however many and varied phenomena, all more or less belonging to the borderlands between chemistry and physics, which may be conveniently considered under the heading of molecular compounds.

100. And I would begin by admitting that no strict definition of molecular, as opposed to atomic, compounds can be given, which shall enable us to assign every disputed case to its proper class. A substance may yield a vapour which is chemically homogeneous below a certain temperature but heterogeneous above this temperature: we cannot fix a limit

<sup>1</sup> See his *Lehrbuch*, Vol. I. pp. 142, 145, 443, &c.: also *Compt. rend.* 58. 510.

for each group of compounds and say, that those which yield vapours homogeneous below this temperature are atomic, while those in the vapour of which dissociation begins below the temperature-limit are molecular.

I would again urge the importance of remembering that when we say that a gas consists of molecules of this or that composition, we refer and can refer only to the average composition of the gas; many molecules may be dissociated into two or more chemically different kinds of matter, other molecules may be aggregated into complex groups. Even in an elementary gas at moderate temperatures some atoms and many groups of molecules are probably present at any moment: the values obtained for the specific gravities of gaseous bromine and iodine, and for gaseous nitrogen dioxide, stannous chloride, and acetic acid well illustrate the gradual nature of the passage from one average molecular state to another<sup>1</sup>.

101. Some chemists would recognise in mixtures of two or more liquids, in solutions of salts, and of gases (e.g.  $\text{CO}_2$ ) in water, the existence of molecular compounds. In such cases the proportions in which the substances are supposed to be combined are very variable. It cannot be correct to speak of a molecule of the mixture of alcohol and water, or of the solution of salt in water, although it may be permissible to regard these liquids as containing groups of molecules of alcohol and water, or of salt and water.

There are other actions wherein small changes in physical conditions suffice to cause changes in the relative quantities of substances combined in definite proportions: for instance, when the substance containing water and sodium phosphate in the proportions  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is heated, it very readily loses water and becomes  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ . If by molecular compound is meant, a loose combination in definite proportions of two or more chemically different kinds of matter so as to produce another kind of matter characterised by fairly definite properties, but readily undergoing change, then

<sup>1</sup> See par. 101, pp. 205, 208—9.

we may certainly say that  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is a molecular compound.

Once more, compounds exist which are characterised by very definite properties, but which, when heated, undergo gradual change into two or more substances, the original compound being gradually re-formed as the vapours cool. Thus the formula  $\text{PCl}_5$  expresses the elementary composition of an undoubted chemical compound; when this solid substance is heated it vaporises, but the vapour can be proved by experiment to contain molecules of  $\text{PCl}_3$  and  $\text{Cl}_2$ , along with undecomposed  $\text{PCl}_5$ . The following numbers shew the gradual progress of the change which occurs:

Calculated sp. gr. of gaseous  $\text{PCl}_5 = 7.2$   
 " " gas consisting of  $\text{PCl}_3 + \text{Cl}_2 = 3.6$  } [air = 1]

Temperature.	Sp. gr. of vapour.	Number of molecules decomposed per 100 molecules of $\text{PCl}_5$ . <sup>1</sup>
182°	5.08	41.7
190	4.99	44.3
200	4.85	48.5
230	4.30	67.4
250	4.00	80.0
274	3.84	87.5
288	3.67	96.2
300	3.65	97.3

The following numbers representing the specific gravities of nitrogen tetroxide at various temperatures exhibit the gradual dissociation of molecules of  $\text{N}_2\text{O}_4$  into molecules of  $\text{NO}_2$ :

<sup>1</sup> Calculated by means of the formula  $p = \frac{100(d-D)}{D}$  where  $p$  = number of molecules decomposed,  $D$  = observed density of gas,  $d$  = theoretical density of vapour supposing no dissociation to occur. This formula assumes that each molecule dissociates into two parts: if each molecule separates into  $a$  parts, the formula is  $p = \frac{100(d-D)}{(a-1)D}$ . See Naumann, *Lehr- und Handbuch der Thermochemie*, pp. 114, 115.

<sup>2</sup> Naumann, *loc. cit.* p. 117.

Temperature.	Sp. gr. of vapour.	Percentage molecular decomposition.	Increase in percentage decomposition for each rise of 10°.
26·7°	2·65	19·96	—
35·4	2·53	25·68	6·5
39·8	2·46	29·23	8·1
49·6	2·27	40·04	11·0
60·2	2·08	52·84	12·1
70·0	1·92	65·57	13·0
80·6	1·86	76·61	10·4
96·0	1·72	84·83	8·8
135·0	1·60	98·69	1·8

As  $\text{N}_2\text{O}_4$  is dark-red and nearly opaque, and  $\text{NO}_2$  is transparent and nearly colourless, the change from one compound to the other can be traced by observing the colour of the heated gas.

A study of the specific gravity of the vapour obtained by heating acetic acid, at different temperatures and pressures, leads to interesting results, some of which are presented in the following table.

Temperature.	Pressure (in millimetres of mercury)	Sp. gr. of vapour (calculated sp. gr. of $\text{C}_2\text{H}_4\text{O}_2$ vapour = 2·08).
120°	760	3·20
125	760	3·20
130	760	3·12
130	60	2·12
130	30	2·10
160	760	2·48
170	760	2·42
220	760	2·15
300	760	2·08

The vapour of acetic acid is denser a few degrees above the boiling point (B.P. = 119°) than at a temperature 100° higher; the specific gravity decreases as the temperature rises (even if the pressure is increased) until it attains a constant value, equal to the theoretical value, at about 220°.

If the density of acetic acid vapour were determined only at 120° and under a pressure of 760 mm. we should deduce the formula  $\text{C}_2\text{H}_4\text{O}_3$  as the molecular formula of this compound. If the density were determined at any temperature



between  $215^{\circ}$  and  $300^{\circ}$  (760 mm.) we should deduce the molecular formula  $C_2H_4O_2$ . Inasmuch as the density gradually decreases as the temperature rises from  $120^{\circ}$  to  $215^{\circ}$ , but remains constant thereafter, and inasmuch as experiment can detect no chemical heterogeneity in the vapour of acetic acid, we conclude that this vapour at low temperatures contains molecules, or molecular groups, the parts of which hold together throughout small temperature-intervals, and that these molecules, or groups, are heavier than those which compose the vapour of the same acid at temperatures about  $100^{\circ}$  above the boiling point of the compound<sup>1</sup>.

If we define a molecular compound, as, a compound the molecules of which may exist in the gaseous state at low temperatures but are gradually decomposed into less dense molecules of the same kind of matter as temperature rises, then we must admit that at temperatures not far above its boiling point acetic acid is a molecular compound.

But if this is so, we evidently have a series of substances, beginning with solutions of salts or gases in water, and proceeding through crystallised solid salts to acetic acid vapour at low temperatures, which connects mechanical mixtures on the one hand with stable gaseous compounds on the other.

It might be urged that we ought not to distinguish between the particles which compose acetic acid vapour at low temperatures and those which form the vapour of the same acid at high temperatures; that if a molecule is 'that small part of a gas the parts of which do not part company when the gas is hot,' then the reasoning which compels us to say, that the molecule of acetic acid vapour at  $220^{\circ}$  is represented by the formula  $C_2H_4O_2$ , likewise compels us to say, that at  $120^{\circ}$  the molecule of this gas is represented by the formula  $C_2H_6O_2$ . The statement that acetic acid at low temperatures is a molecular compound does not appear to me to go against

<sup>1</sup> Another explanation of the anomalies in the sp. gr. of acetic acid vapour has been given by Horstmann; it is based on the hypothesis that the path of a molecule between two collisions is not always a straight line. See O. E. Meyer, *Die Kinetische Theorie der Gase*, pp. 80, 81.

this reasoning; for this statement only implies that at low temperatures the vapour of this acid is composed of particles, of varying masses,—which may be called molecules or molecular groups,—but that these all tend to separate into particles whose composition is represented by the formula  $C_2H_4O_2$ . The  $C_2H_4O_2$  particle is stable throughout so large a range of temperature that we may apply to it and to it only the knowledge we have gained regarding the structure of molecules. It is better not to apply the term molecule to the heavier particles, (1) because they so readily separate into lighter, and stable molecules; (2) because what we know of molecular structure has been gained from, and can therefore only be strictly applied to, the study of molecules which are stable throughout a considerable range of temperature; and (3) because by recognising the possibility of the existence in a gas of groups of molecules, which are not mere mixtures but on the other hand are not to be classed as true molecules, we have the means of explaining, in a general way, many phenomena which at present cannot be explained by any other equally simple hypothesis which is in keeping with the fundamental conceptions of the molecular theory of matter.

That the existence of molecular groups in a gas at low temperatures is in keeping with this theory can readily be shewn. When two gases are at equal temperatures the *mean* kinetic energy of agitation of the molecules must be the same in both; but although the mean kinetic energy is constant for a given temperature, yet the kinetic energy (and hence the temperature) of many molecules may differ from this mean value. If the temperature of the gas is increased, there is an increase not only of the energy of agitation of the molecules as a whole, but also of the energy due to the internal motions of parts of each molecule: as the latter energy increases, a point is reached at which the molecule decomposes into its constituent parts, but these may again unite in some other portion of the mass of gas. As temperature continues to rise a point will come at which molecular decompositions and recompositions are equal in unit of time; the temperature at which this state of matters is reached has been called (by

Naumann and others) the *decomposition-temperature*; from this point onwards the molecular decompositions will exceed the recompositions, until finally there are no recompositions, or these are so few in number that the average state of the gas is fitly described as that of complete decomposition.

Now if we suppose that the gas coming from a liquid at, or near to, its boiling point consists to a great extent of molecular aggregations, we may trace the gradual decomposition of these aggregates into true gaseous molecules, just as we have traced the decomposition of molecules of one kind of matter into those of another kind of matter. The molecular theory of evaporation and condensation almost necessitates the assumption that groups of molecules may exist, and behave for certain small changes in physical conditions, as definite wholes: the facts of spectroscopic science seem also to point to a similar hypothesis<sup>1</sup>.

But why, it might be asked, should not all molecules decompose when heated? It is extremely probable that all molecules are capable of being decomposed by heat. The results of recent experiments on iodine vapour seem to shew that the diatomic molecules of this gas are separated into atoms at high temperatures. The following table exhibits the process of change from  $I_2$  to  $I$ .

*Dissociation of Iodine molecules<sup>2</sup>.*

Temp.	Sp. gr. of vapour.	Percentage decomposition.	Rise of temp.	Increase in percentage decomposition.	Mean increase in decomposition for 100°.
448°	8·74				
680	8·23				
764	8·28				
855	8·07	8·6			
940	7·60	14·5	..... 85°	..... 5·9	..... 6·9
1043	7·01	25·0	..... 103	..... 10·5	..... 10·2
(approxim- 1275	5·82	50·5	..... 232	..... 25·5	..... 11·0
tely) { 1390	5·27	66·2	..... 115	..... 15·7	..... 13·7
1468	5·06	73·1	..... 78	..... 6·9	..... 8·8

<sup>1</sup> In connection with this subject see especially the article 'Constitution of bodies,' by Clerk Maxwell, in the *Encyclopædia Britannica*. (9th Ed.)

<sup>2</sup> Naumann, *Ber.* 13. 1050, using the numbers of Crafts and Meier, *do. do.* 868.

Somewhat similar results have been obtained with bromine. A fact of much interest is disclosed by studying the specific gravities of bromine and chlorine at low and at high temperatures; some of the results of such a study are given in the following table<sup>1</sup>.

*Densities of Bromine and Chlorine.*

Temp. measured in degrees above boiling point of		Specific gravity.		Deviation of sp. gr. from normal, in percentages of latter :—	
BROMINE.	CHLORINE.	BROMINE.	CHLORINE.	BROMINE.	CHLORINE.
40°	40°	5·7115	2·4844	3·381	1·397
60	60	5·6809	2·4810	2·872	1·261
80	80	5·6503	2·4776	2·223	1·122
100	100	5·6197	2·4742	1·719	0·984
120	120	5·5891	2·4708	1·650	0·845
160	160	5·5279	2·4641	0·058	0·571
	200		2·4572		0·290
	240		2·4504		0·000

We have here a phenomenon very analogous to that presented by acetic acid; and if an analogous explanation is to be given, we must suppose that bromine vapour at temperatures from 40 to 140 degrees above the boiling point of this substance contains molecular groups which are slowly decomposed as temperature increases; and that the same holds good of chlorine vapour, only that in this case the molecular groups are relatively lighter, but more stable as regards heat, than those of bromine.

Facts have now been recounted sufficient I think to warrant the adoption of the hypothesis that, even in gases, molecules may hold together in groups, the members of which do not part company throughout more or less extended ranges of temperature and pressure; and if this is so in gases, much more should we expect it to be so in liquids and solids.

102. The hypothesis, by the application of which we hope to find many groups of facts falling into some kind of order, may be broadly stated as consisting in the recognition of a third order of particles more complex than the molecule, as the molecule is more complex than the atom. This hypothesis

<sup>1</sup> Jahns, *Ber.* 16. 1238.

affords no definition of the third order of particles, nor does it always enable us to refer a special case to this order, or to that of molecules. It is a general guide and as such it must be employed; if we refuse its help we shall have to attempt the application of a theory, deduced solely from considerations regarding gases, to explain phenomena presented by solids and liquids; how we may hope to fare in this attempt will be sufficiently indicated by a study of those ingenious pictorial representations which are sometimes called the structural formulæ of mineral compounds.

The properties of crystalline salts which more or less quickly lose water *in vacuo*, and of other solid salts which are unstable under diminished pressures, are explained in a general way in terms of the molecular theory by the aid of the hypothesis of molecular compounds. Most hydrated salts quickly part with 'water of crystallisation' *in vacuo*, some however only slowly; some processes of change proceed in a vacuum very slowly, e.g. ammonium carbamate is very gradually changed into ammonia and carbon dioxide  $[\text{CO} \cdot \text{ONH}_4 \cdot \text{NH}_2 = \text{CO}_2 + 2\text{NH}_3]$ .

Many salts when in solution undergo changes not so marked as those usually called chemical, and yet too definite to be altogether classed as physical; the expression 'dissociation of salts in solution' is sometimes applied to these processes, but the term does not appear to be well chosen. The direction of the change is reversible by altering the condition of temperature. Thus hydrated cobalt chloride crystallises in a rose-red form ( $\text{Co}_2\text{Cl}_4 \cdot 12\text{H}_2\text{O}$ ), while the colour of the dehydrated crystals ( $\text{Co}_2\text{Cl}_4$ ) is blue. If an aqueous solution of the red salt is warmed, the colour slowly becomes darker and finally changes to blue; but the rose-red colour gradually reappears as the liquid cools. The temperature at which the change from hydrated to dehydrated salt occurs is the lower, the less water is present relatively to the amount of salt. A crystal of cobalt chloride growing in a blue-coloured solution can be seen under the microscope to be surrounded by a film of pink liquid, which indicates the existence round the crystal of a zone of liquid containing

relatively less of the salt than the rest of the solution<sup>1</sup>. The solubility of ordinary Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) in water increases until the temperature of  $33^\circ$ — $34^\circ$  is reached, when crystals of the dehydrated salt ( $\text{Na}_2\text{SO}_4$ ) are deposited; the solubility in water of the dehydrated salt decreases from  $18^\circ$  upwards; from these facts, and from the results of many experiments by Löwell<sup>2</sup>, it is almost certain that the particles, the composition of which is represented by the formula  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , separate at  $33^\circ$ — $34^\circ$ , even in presence of water, into  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ .

We seem to be justified in asserting that the solution of a solid in a liquid, if unaccompanied by chemical change or by formation of molecular groups, is always attended with absorption of heat; if, therefore, heat is evolved during solution we conclude that some action other than the mere separation of the molecules of the solid among those of the liquid has occurred. Now if each of the three salts,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{HPO}_4$ , is dissolved in water in such quantity that the solution shall contain the same relative amounts of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  and water, it is found that heat is absorbed during the solution of the two hydrated salts and evolved during the solution of the dehydrated salt. The following table contains the details<sup>3</sup>:

Salt.	Grms. of salt used <sup>4</sup> .	Grms. of water used <sup>4</sup> .	Value of thermal change.
$\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$	16'35	285	- 1024'98 gram-units.
$\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$	12'25	289'1	- 516'22   "   "
$\text{Na}_2\text{HPO}_4$	6'51	294'84	+ 249'88   "   "

In the solution of  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ , less heat is absorbed than in the solution of the salt  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ; and in the solution of  $\text{Na}_2\text{HPO}_4$  a considerable quantity of heat is evolved. These results are at once explained by saying that the negative thermal change which accompanies the solution, pure and

<sup>1</sup> See Lehmann, *loc. cit.* p. 99: see also Potilitzin, *Ber.* 17. 276.

<sup>2</sup> *Ann. Chim. Phys.* [3] 49. 32. See also Watts's *Dict.* 5. 612.

<sup>3</sup> Pfaundler, *Ber.* 4. 775.

<sup>4</sup> In each case 301'35 grms. of solution is formed containing 5'425 per cent. of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ . Specific heat of this solution was constant = 0'972.

simple, of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is partly balanced by the positive thermal change accompanying the fixation of molecules of water by the salt  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  to form  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , and is more than balanced by the positive change accompanying the fixation of a greater number of molecules of water during the solution of the salt  $\text{Na}_2\text{HPO}_4$  also to form the salt  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ <sup>1</sup>. A saturated solution of any of these salts deposits crystals of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  at ordinary temperatures. Hence, from these data, we conclude that a solution of sodium phosphate most probably contains particles whose composition is represented by the formula  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  (and it may be some particles,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  or  $5\text{H}_2\text{O}$ ) but inasmuch as the composition of these particles very readily undergoes change, we prefer to call them molecular groups rather than molecules.

The thermal phenomena attending the solution in water of many other salts, as presented in the following table (taken from Naumann's book), are readily explained by assuming that each solution contains molecular groups of somewhat

*Values of thermal changes attending solution in water of various sulphates.*

Amount of salt employed.	Gram-units of heat evolved or absorbed during solution of					
	dehydrated salt	salt with $1\text{H}_2\text{O}$	salt with $3\text{H}_2\text{O}$	salt with $5\text{H}_2\text{O}$	salt with $7\text{H}_2\text{O}$	salt with $10\text{H}_2\text{O}$
$\text{MgSO}_4$	20,304 +	10,986 +		2388 -	3720 -	
$\text{ZnSO}_4$	18,578 +	9,624 +		2332 -	4148 -	
$\text{CuSO}_4$	16,298 +	9,468 +		2432 -	4260 -	
$\text{MnSO}_4$	14,170 +	8,432 +		470 +		
$\text{CdSO}_4$	10,688 +	6,020 +	3,062 +			
$\text{Na}_2\text{SO}_4$	708 +					18,600 -
$(\text{NH}_4)_2\text{SO}_4$	1950 -					
$\text{K}_2\text{SO}_4$	6340 -					

<sup>1</sup> Calculations based on this assumption, using Pfaundler's numbers, give the following result [Naumann, *Ueber Molekülverbindungen nach festen Verhältnissen*, p. 41]:

The change,  $\text{Na}_2\text{HPO}_4 + 12\text{H}_2\text{O} = \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  is accompanied by evolution of 27,892 gram-units of heat.

The change,  $\text{Na}_2\text{HPO}_4 + 7\text{H}_2\text{O} = \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  is accompanied by evolution of 16,744 gram-units of heat.

The change,  $\text{Na}_2\text{HPO}_4 + 5\text{H}_2\text{O} = \text{Na}_2\text{HPO}_4 \cdot 5\text{H}_2\text{O}$  is accompanied by evolution of 11,148 gram-units of heat.

varying composition, and that that group, the formation of which is attended with the greatest loss of energy (as measured by heat evolved) is present in largest quantity in a solution in much water.

The separation of a solid from solution in a liquid must be attended with evolution of heat. If reactions between salts which form no molecular compounds (or only very unstable compounds) with water at ordinary temperatures, are compared with reactions wherein salts which form comparatively stable molecular compounds with water are concerned, precipitates being produced in both cases, it is found that whereas the former reactions are accompanied by evolution, the latter are rather marked by absorption of heat. Thus, partly from the large negative values of the thermal change accompanying the solution in water of  $\text{PbCl}_2$ ,  $\text{Pb}_2\text{NO}_3$ ,  $\text{NaCl}$ , and  $\text{NaNO}_3$ , and partly from the fact that solutions of these salts deposit crystals of the dehydrated salts at ordinary temperatures, we may conclude that the solutions in question contain either the dehydrated salts or very unstable molecular compounds of these salts with water: on the other hand aqueous solutions of  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{MgSO}_4$  almost certainly contain comparatively stable groups of molecules, composed of molecules of these salts and of water.

The following numbers represent the values of the thermal changes which accompany the formation of some solid salts. (The formula represents quantity of salt in grams in the solution used.)

		Thermal value of change. Gram-units.			
$\frac{\text{Pb} \cdot 2\text{NO}_3}{2}$ (in 2 litres of water) + $\text{NaCl}$ (in 2 litres)	yields solid $\text{PbCl}_2$	...	...	...	1530+.
$\frac{\text{CaCl}_2}{2} + \frac{\text{K}_2\text{CO}_3}{2}$ yields solid $\text{CaCO}_3$	...	...	...	...	450-.
$\frac{\text{CaCl}_2}{2} + \frac{\text{Na}_2\text{CO}_3}{2}$ " $\text{CaCO}_3$	...	...	...	...	570-.
$\frac{\text{MgSO}_4}{2} + \frac{\text{K}_2\text{CO}_3}{2}$ " $\text{MgCO}_3$	..	...	...	...	1050-.

It seems, from these numbers, that the heat absorbed in decomposing the molecular compounds of  $\text{CaCl}_2$ ,  $\text{K}_2\text{CO}_3$ ,



$\text{Na}_2\text{CO}_3$ , and  $\text{MgSO}_4$  with water, is greater than that evolved in the formation, and separation from solutions, of solid  $\text{CaCO}_3$ , or  $\text{MgCO}_3$ .

Granting then that the evolution, or absorption, of heat noticed during solution of a salt in water is to be traced in part to the formation, or non-formation, of complex groups of molecules, it follows from all we know concerning such groups that the fact that the solution of a dehydrated salt is attended with absorption of heat does not of itself prove the non-formation of groups consisting of molecules of the salt and water. Molecular compounds ought to shew a wide range of stability, graduating off on the one side into true compounds and on the other into mixtures. Among the conditions favourable or otherwise to the fixation of molecules of water by molecules of a salt dissolved therein we should regard temperature as very important. A withdrawal of heat from a strong solution might induce such sluggishness of molecular movements as would result in the formation of molecular groups.

Guthrie<sup>1</sup> found that when a strong aqueous solution of common salt is cooled below  $0^\circ$  it deposits crystals having the composition  $\text{NaCl} \cdot 2\text{H}_2\text{O}$ , and that at  $-21^\circ$  the whole liquid sets into a mass of crystals containing salt and water in the proportion expressed by the formula  $2\text{NaCl} \cdot 21\text{H}_2\text{O}$ .

Many *cryohydrates* of other salts have been prepared by Guthrie, e.g.

Formula.	Solidifying point.
$\text{NH}_4\text{Cl} \cdot 12\text{H}_2\text{O}$	$-15^\circ$
$\text{MgSO}_4 \cdot 24\text{H}_2\text{O}$	$-6^\circ$
$\text{Na}_2\text{SO}_4 \cdot 166\text{H}_2\text{O}$	$-0.7^\circ$
$\text{KClO}_3 \cdot 222\text{H}_2\text{O}$	$-0.5^\circ$
$\text{K}_2\text{Cr}_2\text{O}_7 \cdot 292\text{H}_2\text{O}$	$-1^\circ$
$\text{KMnO}_4 \cdot 608\text{H}_2\text{O}$	$-0.37^\circ$
$\text{SrO} \cdot 1463\text{H}_2\text{O}$	$-0.1^\circ$

Each cryohydrate is characterised by definite melting and solidifying points and definite crystalline form; but above

<sup>1</sup> *Phil. Mag.* [4] 49. 1 and 206; [5] 1. 49, 354, 446; 2. 212; 6. 35, 105. For a description of some alcoholates, e.g.  $\text{MgCl}_2 \cdot 6\text{C}_2\text{H}_5\text{OH}$ , see Simon, *J. pract. Chemie* (2) 20. 371.

a certain (low) temperature each separates into molecules of water and salt, or of water and hydrated salt. The properties, and the phenomena attending the formation, of cryohydrates, are evidently in keeping with the special phase of the molecular theory which we are now considering<sup>1</sup>.

From the results of Lehmann's microscopic studies<sup>2</sup> on the formation of crystals of hydrated ferrous chloride, cobaltous chloride, and cupric chloride it appears certain that a solution from which crystals, now of a more hydrated now of a less hydrated salt, separate, as temperature varies, does not contain at a fixed temperature only the one hydrate and at another temperature only the other hydrate. As temperature slowly rises the molecular groups tend to fall in pieces and so the liquid becomes poorer in particles of the relatively most hydrated salt; on cooling, the conditions are reversed, and the liquid becomes poorer in particles of the least hydrated salt. Lehmann considers the three cases (1) the liquid is equally saturated for the hydrate rich in water and for that poorer in water; (2) the liquid contains rather more of one hydrate than of the other; (3) the liquid is concentrated as regards one hydrate, but dilute as regards the other. He shews that, as temperature slowly increases, in the first case, crystals of both hydrates grow simultaneously and at the same rate until the spheres<sup>3</sup> of the crystals touch, when growth is almost entirely stopped; in the second case, both kinds of crystals grow, but one kind more quickly than the other, then both grow at the same rate, and then the second kind of crystals grow more rapidly than the first; in the third

<sup>1</sup> The hypothesis of the formation at low temperatures of complex unstable molecular groups helps us to understand some of the phenomena presented by variations in the rate of chemical changes under abnormal circumstances; this subject will be considered in the second part of this work. The same hypothesis also throws light on the action of concentrated and dilute hydrochloric acid on antimony sulphide: this is fully considered under 'Thermal Chemistry,' see *post*, chap. IV. section 1.

<sup>2</sup> *Loc. cit.* pp. 100—103.

<sup>3</sup> Lehmann's term is 'der Hof des Krystalles:' each crystal, he says, can be seen under the microscope to be surrounded by a liquid film, from which it draws its supplies of solid matter; this is the *Hof* or sphere of the crystal.

case, those crystals which are present in the liquid in greater quantity grow rapidly, and the others dissolve rapidly, so that the dissolving crystals appear to pass directly into crystals of the other hydrate.

The definite form, solubility, temperature of formation, &c. of each kind of crystal formed in these experiments conducted by Lehmann prevent us from regarding the various hydrated salts as mere mixtures of ice and salt; on the other hand, the extremely small variations in temperature, or relative amount of water and salt, necessary to cause change from one crystal to another, equally prevent us from attempting to explain the properties of each hydrate as wholly, or almost wholly, conditioned by the mutual interactions of atoms within the molecule: we seem forced to adopt the hypothesis of molecular compounds.

The researches of Graham on colloidal and crystalloidal substances are of the utmost importance as regards the hypothesis we are considering; to understand the importance of Graham's work it is necessary carefully to study the whole series of papers on liquid diffusion which he communicated to the Royal Society<sup>1</sup>. Graham<sup>2</sup> found that certain substances when in solution pass very quickly through wet animal or vegetable membranes, while others are scarcely, if at all, diffusible through the same septa. The more diffusible bodies Graham called *crystalloids*, the less diffusible he called *colloids*. Colloidal substances e.g. albumen, hydrated alumina or stannic oxide, &c. are very inert chemically considered, but at the same time they are affected by the smallest changes in their environment e.g. slight alterations of temperature cause marked changes in their properties; they are easily permeated by diffusible crystalloidal substances, to which, says Graham, they give up water, 'molecule by molecule'; 'their existence 'is a continual metastasis'. Ice, which under ordinary conditions of formation is crystalloidal, when formed in contact with water at 0° possesses those properties which characterise

<sup>1</sup> Happily Graham's papers have been collected and published by the late Drs Angus Smith and James Young.

<sup>2</sup> *Phil. Trans.* for 1861, 185.

colloids; 'can any facts more strikingly illustrate the maxim 'that in nature there are no abrupt transitions, and that 'distinctions of class are never absolute?' (Graham).

The marked differences between the properties of colloids and crystalloids are associated, in the opinion of Graham, with differences of molecular structure. He regarded the reacting unit of a colloid as probably formed by the coalescence of a large number of molecules, hence the marked instability, and at the same time chemical inertness, which characterise the class of colloidal substances.

Some very interesting observations have been made by van Bemmelen<sup>1</sup> on the absorption of acids and salts by hydrated oxides. When the hydrated dioxide of tin, silicon, or manganese is shaken with an aqueous solution of a mineral acid, or a salt such as potassium sulphate or sodium chloride, a definite quantity of the acid or salt is absorbed by the oxide; the amount absorbed is dependent on the nature of the hydrated oxide and the nature of the acid or salt, on the relative masses of oxide, acid, or salt, and on the amount of water present. The substances which exhibit this action are characterised by the readiness with which the change from hydrated to dehydrated salt and *vice versa* occurs; thus the hydrates  $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ ,  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ , and  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  part with water when placed over sulphuric acid, and the oxides absorb water when placed in a moist atmosphere. The amount of water absorbed by any one of the dehydrated oxides depends in part on its physical state; if the oxide is strongly heated it absorbs less water than if dried over sulphuric acid *in vacuo*<sup>2</sup>; the 'looser' the aggregation of the particles, the greater the quantity of water absorbed by the oxide.

In some cases, e.g. the hydrate  $\text{SiO}_2 \cdot 4\text{H}_2\text{O}$ , the amount of acid or salt withdrawn from an aqueous solution was

<sup>1</sup> *J. für prakt. Chemie* [2] 23. 324; see also 26. 227.

<sup>2</sup> Graham [*Brit. Ass. Reports for 1834*, 579] called attention to the difference between strongly heated calcium sulphate and the same substance 'in a state for setting;' but, says Graham, "this is a department of corpuscular philosophy which stands much in want of further development."

found to be equivalent to the amount of water loosely held by the oxide, i.e. the water removed by drying over sulphuric acid *in vacuo*. In other cases, e.g.  $\text{SnO}_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{SnO}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{SnO}_2 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{MnO}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{MnO}_2 \cdot 2\text{H}_2\text{O}$ , the amount of salt, &c., withdrawn by the hydrate from solution was greater than the quantity equivalent to the loosely-held water of the hydrate. As the amount of water which an oxide absorbs from a moist atmosphere was found to vary with the physical aggregation of that oxide, so the amount of salt or acid absorbed by the hydrated oxide was found to shew analogous variations: this is specially worked out in detail by van Bemmelen for the action of metastannic acid on aqueous solutions of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ , and  $\text{KNO}_3$ .

If these actions are to be classed as purely physical, we should not expect to find a definite limit to the amount of salt or acid absorbed by each hydrated oxide; but van Bemmelen's researches shew that the process tends to the establishment of an equilibrium between acid (or salt), water, and hydrated oxide, that this condition is attained slowly, and that it is affected by the relative masses of the acting substances in the original system. Thus less acid (or salt) is absorbed from a very dilute than from a more concentrated solution, but the amount of acid, &c., absorbed increases much more slowly than the increase in the concentration of the solution of acid or salt. The final equilibrium is not disturbed by addition of more acid (or salt) solution of the same degree of concentration as that surrounding the hydrated dioxide, but if the added solution is relatively richer in acid or salt than the liquid surrounding the dioxide, then the equilibrium is overthrown and the absorption of acid, &c., begins again and proceeds till a second condition of equilibrium is established.

Some hydrated oxides not only absorb, but also partially decompose salts: e.g.  $\text{MnO}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  when shaken with an aqueous solution of  $\text{K}_2\text{SO}_4$  absorbs a definite amount of the latter and at the same time separates part of it into  $\text{KOH}$  and  $\text{H}_2\text{SO}_4$ . Again, one salt is sometimes absorbed in pre-

ference to another, thus if  $\text{MnO}_2 \cdot x\text{H}_2\text{O}$  is shaken in contact with  $\text{H}_2\text{SO}_4$ , washed, and again shaken in contact with an aqueous solution of  $\text{K}_2\text{SO}_4$ , a portion of the  $\text{H}_2\text{SO}_4$  which had been absorbed by the hydrated oxide is replaced by  $\text{K}_2\text{SO}_4$ ; again, if  $\text{SiO}_2 \cdot 4\text{H}_2\text{O}$  is allowed to absorb  $\text{Al}_2\text{Cl}_6$ , is then washed till the washings no longer contain chlorine, and is finally shaken with an aqueous solution of  $\text{KCl}$ , it is found that some of the  $\text{KCl}$  has been absorbed and some of the  $\text{Al}_2\text{Cl}_6$  has passed into the surrounding liquid.

These substances, investigated by van Bemmelen, whether they be called compounds or loose combinations of salt (or acid) and hydrated oxide, can scarcely be regarded as composed of molecules each built up of atoms of metal, oxygen, hydrogen, and the elements of acid or salt, but rather as composed of molecular groups each constituted by the coalescence of molecules of acid (or salt), water, and metallic oxide, the number of such molecules in each group or 'reacting unit' being variable within certain limits. The properties of many of the salts of the 'weaker' acids—e.g. carbonic, boric, and sulphurous—are regarded by van Bemmelen as explicable in terms of the general hypothesis of molecular compounds; he would regard the reacting units of these salts as molecular groups, more stable than those which compose the peculiar class of bodies just described, but less stable than the true chemical molecule.

103. In his second paper (*loc. cit.*) van Bemmelen has more particularly studied hydrated beryllium oxide  $\text{BeO} \cdot x\text{H}_2\text{O}$ . He shews that two varieties of this oxide exist, viz. a gelatinous and a granular form, that the former alone exhibits the property of absorbing acids and salts from aqueous solutions, and also that the action of heat on the two hydrates is different. After heating to  $220^\circ$  the granular hydrate has lost  $0.5 \text{ H}_2\text{O}$ , and is now much altered in properties. This fact—and others analogous to this are known—seems to shew that by the application of energy from without the system the parts of a loose molecular group may be caused to react so as to bring about a marked change in the properties of the body composed of such groups. In other words, the comparative

readiness with which definite chemical changes may be started among the constituents of a molecular group appears to shew that although these constituents are held together but loosely, nevertheless they are not merely mixed. Thus,  $\text{As}(\text{CH}_3)_2\text{Cl}$  combines with  $\text{Cl}_2$  to form  $\text{As}(\text{CH}_3)_2\text{Cl}_2$ ; when this compound is heated it yields  $\text{As}(\text{CH}_3)\text{Cl}_2 + \text{CH}_3\text{Cl}$ ; then  $\text{As}(\text{CH}_3)\text{Cl}_2$  readily takes up  $\text{Cl}_2$  to form  $\text{As}(\text{CH}_3)\text{Cl}_3$ , which on being heated separates into  $\text{AsCl}_3 + \text{CH}_3\text{Cl}$ . Now on account of their properties some of these compounds must be classed as molecular, yet under the influence of heat the parts of the molecular groups mutually act and react in a way analogous to, if not identical with, that characteristic of chemical change. But such phenomena as these are exactly what might be expected from the hypothesis of molecular compounds; if these bodies are formed of groups of molecules we should expect that reactions between these groups would, in many cases, easily occur and result in the production of new, less complex, groups, or, it may be, new molecules. That a substance is found to behave in a definite manner under the influence of this or that reagent cannot be regarded as sufficient evidence for classing it among atomic rather than molecular compounds. Thus the observation recorded by R. W. Atkinson<sup>1</sup> regarding the identity of the salts produced by mixing  $\text{SbCl}_3$  and  $3\text{KBr}$ , and  $\text{SbBr}_3$  and  $3\text{KCl}$ , cannot be regarded as proving that the product of these actions is built up of molecules represented by the formula  $n\text{SbCl}_3\text{Br}_3\text{K}_3$ , the properties of which are conditioned only by the mutual interactions of the atoms Sb, Cl, Br, and K. Regarded however as a contribution towards solving the questions suggested by the term molecular compounds, the observations made by Atkinson are of interest, as shewing how possible it is to obtain substances which behave in some respects as molecular and in other respects as atomic compounds. It cannot be too strongly insisted on that no hypothesis has been proposed regarding molecular compounds which furnishes us with a definition of the class 'molecular', or puts into our hands

<sup>1</sup> *C. S. Journal, Trans.* for 1893. 289.

an instrument for determining whether a given compound belongs to this class or to the class of atomic compounds. What the hypothesis does is to negative the notion that the properties of all compounds are to be explained by the conception of actions and reactions between atoms which together constitute a molecule, to restrict the application of the theory of valency to gaseous compounds, and to open a path for future research by insisting on the complexity of chemical phenomena, and the folly of attempting to explain all in terms of a favourite theory.

But the consideration of molecular compounds leads to the discussion of questions which properly belong to chemical kinetics; we cannot separate these bodies from their environment; they are members of a system which is continually undergoing change and the comparative stability of which is the result of never ceasing action and reaction between its parts. Chemistry is not a collection of facts regarding the crystalline form, melting points, boiling points, specific gravities, &c., &c., of so-called pure elements or compounds; it is rather the orderly and regulated study of the changes which matter undergoes and which result in more or less profound modifications in the properties of the changing bodies.

A great advance has certainly been made by replacing the conception of a molecule as an undefined quantity of matter constructed of groups of atoms more or less loosely and vaguely arranged, by that conception of the molecule which regards it as a definite and definable quantity of matter, built up of atoms arranged in an orderly manner, and exhibiting functions dependent on the nature, arrangement, and mutual interactions of these atoms. Among the functions of these molecules we must however, I think, place the power of combining with other molecules to form more or less complex groups, less stable than the molecules of a gas, and not so sharply defined from other groups as the molecule of one compound is from that of another. Although the explanation of the properties of molecular compounds is not to be brought within the scope of the theory of valency, nevertheless if we



regard the formation (or nonformation), and the relative stabilities, of such compounds as functions of all the molecules concerned in their synthesis, we can see that the valencies of the elementary atoms must be important factors in determining the production of molecular compounds<sup>1</sup>.

<sup>1</sup> In connection with this subject compare van't Hoff's *Ansichten über die Organische Chemie*, pp. 4, 5.

## CHAPTER III.

### THE PERIODIC LAW.

104. ATTEMPTS have from time to time been made throughout the preceding 50 or 60 years to trace connections between the atomic weights and the general properties of groups of elements.

Soon after the appearance of Dalton's *New System of Chemical Philosophy*, an hypothesis was promulgated by Prout to the effect that the atomic weights of the elements are whole multiples of that of hydrogen; but the researches of Berzelius, Marignac and Stas shewed that this hypothesis was untenable. A modification of Prout's hypothesis was made by Dumas which appears to have a fair probability in its favour.

Gmelin, Dumas, Gladstone, Cooke, Kremers, Pettenkofer, Odling, and especially Newlands<sup>1</sup> (who was among the earliest workers in this field,) have drawn attention to points of connection between the properties and the atomic weights of elements.

It is however especially to Mendeleeff<sup>2</sup> that we owe the systematic correlation of the atomic weights with the chemical and physical properties of the elements.

Lothar Meyer<sup>3</sup> has also made important contributions to the same subject, and in his *Modernen Theorien* he has

<sup>1</sup> *Chem. News*, 7. 70, and 10. 59, 94. 12. 83, 94. 13. 113. &c. Newlands' contributions to this subject have been gathered together and published in a small volume entitled 'On the Discovery of the Periodic Law' [Spon. 1884].

<sup>2</sup> *Annalen*, Suppl. Bd. 8. 133. See also *Chem. News*, Vols. 40 and 41.

<sup>3</sup> *Annalen*, Suppl. Bd. 5. 129, and 7. 354 &c.

gathered together the more important facts which have been established concerning the relation in question.

105. We may confidently say that a large probability has been established in favour of the hypothesis that the properties of the elements, and of the compounds of each element, are periodic functions of the atomic weights of the elements. Lothar Meyer puts the general statement of the "*Periodic Law*" in this form<sup>1</sup>; 'if the elements are arranged in order of 'increasing atomic weights, the properties of these elements 'vary from member to member of the series, but return more 'or less nearly to the same value at certain fixed points in 'the series'.

Let the elements be arranged in the order of their atomic weights; let this list of elements be (broadly) divided into series of sevens; let the members of the second series be placed under those of the first, those of the third under those of the second, and so on; and let the elements contained in a vertical column be called a *group*, those in a horizontal column being called a *series*. Then taking an element R, and calling the elements next before and after it in the same series X and Y respectively, and those in corresponding positions in the same group R' and R'', we may say that

atomic weight, density, and atomic volume of R =

$$\frac{\text{atomic wt., density, atomic vol. of X} + \text{the values of same constants for Y}}{2}$$

and also that atomic weight, &c. of R =

$$\frac{\text{atomic weight, \&c. of R'} + \text{constants of R''}}{2}.$$

In the arrangement of the elements just described, each *group* corresponds, for the most part, with a natural family. This is more clearly shewn, and the relations between the atomic weights and the properties of the elements are more distinctly developed if certain gaps are supposed to exist in the list of elements. The following table<sup>2</sup> exhibits this arrangement of the elements.

<sup>1</sup> *Die Modernen Theorien*, 4th Ed. p. 136.

<sup>2</sup> Taken from a paper by B. Brauner in *C. S. Journal Trans.* for 1882. 78: atomic weights are stated in round numbers.

GROUPS									
	I	II	III	IV	V	VI	VII	VIII	
<i>Series</i>	$R_3O$	$R_3O_3$	$R_3O_3$	$R_3O_4$	$R_3O_5$	$R_3O_6$	$R_3O_7$	$[R_3O_8]$	
1	H=1								
2	Li=7	Be=9	B=11	C=12	N=14	O=16	F=19	—	
3	Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35.5	{ Fe=56 Co=59	Ni=58.6 Cu=63
4	K=39	Ca=40	Sc=44	Ti=48	V=51	Cr=52	Mn=55		
5	(Cu=63)	Zn=65	Ga=69	(? 72)	As=75	Se=79	Br=80	{ Rh=104 Pd=106	Ru=104.5 Ag=108
6	Rb=85	Sr=87	Y=89	Zr=90	Nb=94	Mo=96	(? 100)		
7	(Ag=108)	Cd=112	In=114	Sn=118	Sb=120	(? Te=126)	I=127	? 152—156 4 Elements ?	{ Ir=192.5 Pt=194
8	Cs=133	Ba=137	La=139	Ce=141	Di=144	? 149	? 150		
9	← ? 4 Elements 156 to 162 ?			Er=166			? 167	{ Os=193 Au=196	
10	? 170	? 172	Yb=173	? 178	Ta=182	W=184	? 169		
11	(Au=196)	Hg=200	Tl=204	Pb=207	Bi=209	← ? 2 Elements 212 to 220 ?			
12	← ? 3 Elements 220 to 230 ?			Th=232	? 237	U=240	? 245		

106. Before giving a detailed explanation of this table let us meanwhile gather together some of the best established generalisations concerning the periodic connection of properties and atomic weights of the elements.

A phenomenon is said to be periodic when, if the conditioning circumstances vary continuously, it repeats itself at definite intervals. The variable under consideration is the atomic weight, the phenomenon to be examined is the nature of the chemical element and its compounds. Although it is not as yet possible to state quantitatively the nature of the periodic function which connects the atomic weights and general properties of the elements, it may nevertheless be established that the function in question is periodic. For this purpose it will be necessary to break up the phenomenon 'nature of the chemical element and its compounds' and to endeavour to shew that the malleability, ductility, atomic volume, power of forming oxides (or chlorides) of definite composition, position in electrical series, &c. of the elements do vary periodically with variations in the atomic weights of these elements<sup>1</sup>.

107. *Atomic volume.* The quotient obtained by dividing the specific gravity of an element, in the solid form, by its atomic weight is called the atomic volume of that element. This quotient expresses the volume, in cubic centimetres, occupied by an amount of the solid element, in grams, proportional to the atomic weight of that element.

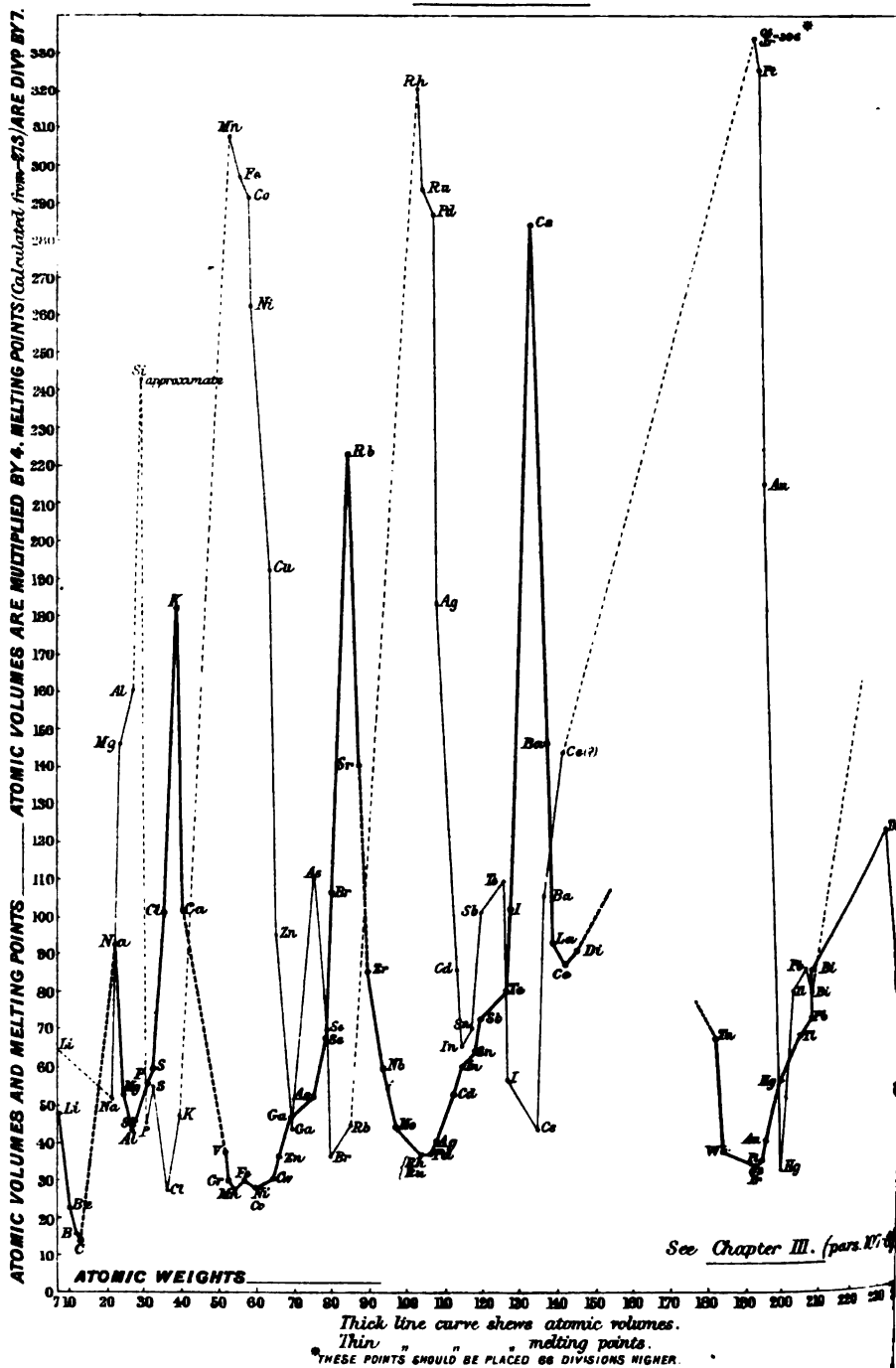
Arranging the elements in order of increasing atomic weights it is found that the value for atomic volume reaches its first maximum at lithium, that it then diminishes through beryllium, boron, &c. and again increases through carbon, &c. reaching a second maximum at sodium; the other maxima occur at potassium, rubidium, and cæsium.

The periodic nature of the connection between atomic volumes and atomic weights becomes very apparent when the

<sup>1</sup> For greater details on this point see L. Meyer, *Die Modernen Theorien*, 4th Ed. pp. 139—173, of which this and the few following pages must be regarded as an abstract.



# THE PERIODIC LAW.



magnitudes of those quantities are graphically represented as is done on the plate facing this page<sup>1</sup>.

The maximum points on the curve are seen to be occupied by metals of low specific gravity, while the minimum points are occupied by heavy metals.

The position of an element on the curve, with reference to the preceding and succeeding elements, appears to exert a marked influence on the properties of the element in question. Thus phosphorus and magnesium on the one hand, and calcium and chlorine on the other, have nearly equal atomic volumes; phosphorus and chlorine are followed by elements the atomic volumes of which are larger than their own (i.e. are situated on ascending portions of the curve), whereas magnesium and calcium are followed by elements having atomic volumes smaller than their own (i.e. are situated on descending portions of the curve).

The ductile metals are placed at or near to maximum and minimum points on the curve; those of low specific gravity occurring at, and immediately after maximum points, and those of high specific gravity at, and immediately after minimum points. The brittle heavy metals occur in sections 4, 5, and 7 immediately before the minimum points<sup>2</sup>.

The elements on the descending parts of sections 2 and 3 of the atomic volume curve are electropositive and form basic hydroxides; those on the ascending portions of the same sections are electronegative and form acid hydroxides. Sections 4 and 5 each contain four groups of elements arranged in accordance with their negative or positive character. Electropositive elements occur on the first portions of the descending curve in each of these sections (K, Ca; Rb, Sr); these are

<sup>1</sup> Only those elements the specific gravities of which in the solid state have been directly determined are included in the curve; want of data is indicated by a broken line.

<sup>2</sup> A section of the curve means the part situated between two maxima; section 1 includes hydrogen only, section 2 extends from lithium to sodium, &c. There are probably several unknown elements with atomic weights greater than that of didymium and smaller than that of tantalum; the curve, if complete, would probably be marked by a sixth maximum point between cæsium and thorium, this part of the curve is therefore said to comprise two sections (6 and 7).



followed by a group of comparatively negative elements (V, Cr, Mn; Zr, Nb, Mo, Rh, Ru); these again by positive elements (Fe, Ni, Co, Cu, Zn, Ga; Pd, Ag, Cd, In); and after these comes a group of negative and acid-forming elements situated on the ascending part of the curve in each section (As, Se, Br; [Sn], Sb, Te, I). Sections 6 and 7 are too incomplete to allow of definite conclusions being drawn regarding the positive or negative character of the elements situated thereon.

108. *Fusibility.* The melting points of several elements have been determined by various observers<sup>1</sup>; of late especially by Carnelley<sup>2</sup>, who has shewn that the fusibility of the elements varies periodically with their atomic weights. The thin line<sup>3</sup> curve on the plate facing p. 227 graphically exhibits this connection.

A connection may be traced between the positions of an element on the curve of atomic volumes and on that of fusibility; as a rule, only those elements which are situated on ascending portions of the former curve, are easily fusible. Generalisations have also been made concerning the connections between the atomic weights of groups of elements and the melting points of these elements and some of their analogous compounds<sup>4</sup>. Thus the melting points of the haloid salts of the metals in group II. (see table on p. 225) are considerably higher than those of the corresponding salts of the metals of group III.

<i>e.g.</i>	MgCl <sub>2</sub>	MgBr <sub>2</sub>	CaCl <sub>2</sub>	CaBr <sub>2</sub>	CaI <sub>2</sub>	SrCl <sub>2</sub>	SrBr <sub>2</sub>	SrI <sub>2</sub>
M.P.	708	695	719	676	631	825	630	507
but	Al <sub>2</sub> Cl <sub>3</sub>	Al <sub>2</sub> Br <sub>3</sub>	Al <sub>2</sub> I <sub>3</sub>					
M.P.	very low	90	185.					

<sup>1</sup> See *Constants of Nature*, Part I. and Supplement to do. Also L. Meyer, *loc. cit.* pp. 145, 6.

<sup>2</sup> *Phil. Mag.* [5] 8. 315 *et seq.* This paper contains a good *resumé* of the *periodic law*.

<sup>3</sup> The values of the melting points used in preparing this curve are taken for the most part from Carnelley's paper. The data are meagre, hence many gaps occur in the curve (indicated by the broken lines); many of the numbers, especially those for elements at and near to maximum points, must be regarded as only roughly approximate to the true values.

<sup>4</sup> See Williams and Carnelley, *C. S. Journal Trans.* for 1879. 563; 1880. 125.

Carnelley<sup>1</sup> found the melting point of beryllium chloride to lie between 585 and 617°, hence he concluded that beryllium belongs to group II. and that the formula of its chloride is  $\text{BeCl}_2$  ( $\text{Be} = 9.1$ ), and not  $\text{BeCl}_3$  or  $\text{Be}_2\text{Cl}_6$  ( $\text{Be} = 13.15$ )<sup>2</sup>. The data, so far as obtained, concerning the boiling points, crystalline forms, and expansion by heat of the elements, indicate that the connection between those constants and the atomic weights of the elements is of a periodic character<sup>3</sup>.

109. Reasoning from certain assumptions as to the vibrations of the particles of solid elements at their melting points, Pictet<sup>4</sup> has concluded that  $\alpha \cdot T \cdot \sqrt[3]{V} = \text{constant}$ ; where  $\alpha$  = coefficient of linear expansion,  $T$  = melting point in absolute temperature, and  $V$  = atomic volume, of any element. This generalisation holds good for most of the elements for which sufficient data have been obtained; the value of Pictet's constant varies from about 3.9 to about 4.9<sup>5</sup>.

Hartley<sup>6</sup> has shewn that the ultra-violet spectra of elements of the same series shew fairly marked analogies as regards general character; the spectra hitherto obtained do not permit him to affirm, or deny, the existence of numerical relations between the different groups of lines, sufficient to establish a definite periodic connection between the atomic weights of the elements and the wave-lengths of the lines in the elementary spectra.

That there exists a well-marked connection, of periodic character, between the atomic weights, and the heats of combination of the elements with chlorine, bromine and iodine has been shewn by A. P. Laurie<sup>7</sup>. The data are somewhat

<sup>1</sup> *Proc. R. S.* 29. 190. According to more recent determinations by Nilson and Pettersson (*Ber.* 17. 987), the melting point of beryllium chloride is 100° to 150° lower than the temperature given by Carnelley.

<sup>2</sup> See forward, par. 111.

<sup>3</sup> For details see L. Meyer, *loc. cit.* pp. 150—151.

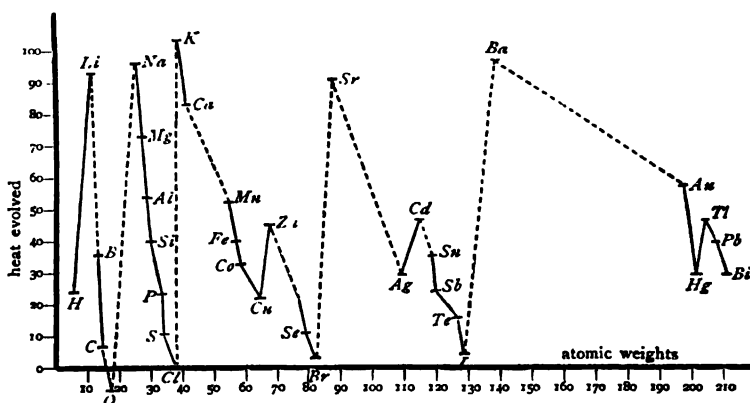
<sup>4</sup> *Compt. rend.* 38. 855.

<sup>5</sup> For data see L. Meyer, *loc. cit.* pp. 154—156.

<sup>6</sup> *C. S. Journal Trans.* for 1883. 84: permanent photographs of the ultra-violet spectra of various elements are given in this paper. See also *ibid.* *Trans.* for 1883. 390.

<sup>7</sup> *Phil. Mag.* (5) 15. 42. For data shewing that some of the physical

scanty. The accompanying curve has been constructed from the values given by Thomsen, in his *Thermochemischen Untersuchungen*, for the reaction  $[M, Cl]$ , the quantities of heat being stated in kilogram-units.



110. Having thus established the existence of a connection, distinctly of a periodic character, between the atomic weights and the general nature of the elements, we may proceed to consider the more important applications of the periodic law. This consideration will also serve more fully to elucidate the meaning of the law.

The law has been applied to predict the properties of unknown elements. In the nomenclature of unknown elements Mendeleeff employs Sanscrit prefixes, *eka*, *dui*, *tri*, &c. Thus looking at group IV. (see table, p. 225), titanium, zirconium and cerium, supposing those elements unknown, would be named *eka-carbon*, *dui-carbon* and *tri-carbon*. At the time of Mendeleeff's earliest publication there was no element known which could be placed opposite the atomic weight 69 in group III., nor any which could be placed opposite the atomic weight 44 in the same group. The former of these hypothetical elements Mendeleeff named *eka-alumi-*

properties of compounds, *e.g.* melting and boiling points, vary periodically with variations in the atomic weights of the constituent elements, see Carnelley, *Phil. Mag.* [5] 8. 368—70.

nium, the latter he called *eka-boron*. The properties of *eka-aluminium* were predicted by Mendelejeff from considering the position of the element in the same group as, and interposed between, aluminium and indium, and in the same series as, and following after, zinc. In 1875 a new metal was discovered by L. de Boisbaudran. The following table contains, in parallel columns, the leading properties of this metal, and those enumerated by Mendelejeff as characteristic of *eka-aluminium*: there can be no doubt that the hypothetical metal of Mendelejeff and the *gallium* of de Boisbaudran are one and the same element.

*Eka-aluminium.*

Readily obtained by reduction.  
Melting point low. Sp. gr. = 5.9.  
Not acted on by air.  
Will decompose water at a red heat.  
Slowly attacked by acids or alkalis.  
Will form a potassium alum more soluble, but less easily crystallisable, than the corresponding aluminium salt.  
Oxide =  $\text{El}_2\text{O}_3$ . Chloride =  $\text{El}_2\text{Cl}_6$ .  
Atomic weight about 69.

*Gallium.*

Readily obtained by electrolysing alkaline solutions.  
M.P. =  $30.15^\circ$ . Sp. gr. = 5.93.  
Non-volatile, and but superficially oxidised in air at bright red heat.  
Decomposes water at high temperatures. Soluble in hot hydrochloric acid, scarcely attacked by cold nitric acid; soluble in caustic potash.  
Forms a well-defined alum.  
Chloride =  $\text{Ga}_2\text{Cl}_6$ . Oxide =  $\text{Ga}_2\text{O}_3$ .  
Atomic weight = 69.7.

*Eka-boron* belongs to group III.; the general formula for the oxides of the members of this group is  $\text{R}_2\text{O}_3$ ; in its properties *eka-boron* ought to be related to aluminium as calcium is to magnesium, and as titanium is to silicon. The atomic weight of *eka-boron* must be about 43—46, inasmuch as it follows K (39) and Ca (40), and is followed by Ti (48) and V (51). Reasoning from these data, Mendelejeff<sup>1</sup> predicted certain properties as characteristic of *eka-boron* and its salts. Some of these are placed in parallel columns with a description of the properties of the metal *scandium*<sup>2</sup>, discovered in 1879 by Nilson.

<sup>1</sup> See translation of Mendelejeff's paper in *Chem. News*, 41. pp. 71—72.

<sup>2</sup> *Ber.* 18. 1439. See also Cleve, *Ber.* 12. 2264; and *Compt. rend.* 89. 419, (abstract of latter paper in *C. S. Journal* for 1880. 8, is useful).

*Eka-boron.*

Atomic weight about 44.  
 Oxide  $\text{Eb}_2\text{O}_3$ , soluble in acids; sp. gr. about 3.5; analogous with but more basic than  $\text{Al}_2\text{O}_3$ ; less basic than  $\text{MgO}$ ; insoluble in alkalis.  
 Salts of Eb colourless, and yield gelatinous precipitates with  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{Na}_2\text{HPO}_4$ , &c.  
 Sulphate  $\text{Eb}_2 \cdot 3\text{SO}_4$  will form a double salt with  $\text{K}_2\text{SO}_4$ , probably not isomorphous with the alums.  
 Chloride  $\text{EbCl}_3$  or  $\text{Eb}_2\text{Cl}_4$ , sp. gr. about 2, less volatile than  $\text{Al}_2\text{Cl}_6$ .

*Scandium.*

Atomic weight = 44.  
 Oxide  $\text{Sc}_2\text{O}_3$ ; sp. gr. = 3.8; soluble in strong acids; analogous with but more decidedly basic than  $\text{Al}_2\text{O}_3$ ; insoluble in alkalis.  
 Solutions of Sc salts colourless and yield gelatinous precipitates with  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{HPO}_4$ .  
 Sulphate  $\text{Sc}_2 \cdot 3\text{SO}_4$  forms a double salt, not an alum,  $\text{Sc}_23\text{SO}_4 \cdot 2\text{K}_2\text{SO}_4$ .

There is a gap in group IV. series 5. *Eka-silicon* comes in the group which comprises Si, Sn, and Pb, and in the series including Ga, and As. This hypothetical element ought also to shew analogies with other elements; thus,



From the position of *eka-silicon*<sup>1</sup> Mendelejeff concludes that it will be a grey metal, obtained by reducing the oxide by sodium, fusible with difficulty; it will decompose steam very slowly, will be scarcely acted on by acids, but easily by alkalis. The oxide,  $\text{EsO}_2$ , (sp. gr. about 4.7) will be obtainable by burning the metal in air, it will resemble  $\text{TiO}_2$ , but will be less basic than this oxide, although more basic than  $\text{SiO}_2$ ; the hydroxide will be soluble in acids, but the solution will be easily decomposed yielding an insoluble metahydroxide. The oxide will yield a series of double fluorides  $\text{M}_2\text{EsF}_6$  (M = alkali metal) isomorphous with the corresponding salts of Si, Ti, Zn and Sn. The fluoride  $\text{EsF}_4$  will not be gaseous; the chloride  $\text{EsCl}_4$  will be a volatile liquid boiling at about  $100^\circ$ . *Eka-silicon* will form volatile organo-compounds. The new element will probably occur, along with several other unknown elements, in those complex minerals which contain titanium and niobium. It may be separated from the former metal by taking advantage of the difference between

<sup>1</sup> See *Chem. News*, 41. 83.

the boiling points of the two chlorides ( $\text{TiCl}_4$ , B.P. =  $136^\circ$ ). Mendelejeff thinks that the discrepancies between the numbers obtained by Rose, Pierre and others as representing the atomic weight of titanium may possibly have been due to the unsuspected presence of  $\text{EsCl}_4$  in the  $\text{TiCl}_4$  analysed by them.

The discovery of *eka-silicon* is still in the future; yet looking to the history of gallium and scandium we may almost consider *eka-silicon* as one of the known elements.

III. The periodic law has also been successfully used as a guide in the comparative study of the properties of elements already known.

To which group of elements does beryllium belong? Is the formula of the oxide  $\text{BeO}$  or  $\text{Be}_2\text{O}_3$ , and of the chloride  $\text{BeCl}_2$  or  $\text{BeCl}_3$ ? Is the atomic weight of beryllium 9 or 13.5?

The arrangement of the elements in accordance with the periodic law seems to necessitate the placing of beryllium in group II.; but recently amassed experimental evidence suggests, in the opinion of some chemists, necessitates in that of others, that this metal should be placed in the group characterised by the power of forming an oxide  $\text{R}_2\text{O}_3$ . The atomic weight of beryllium =  $n \cdot 9 \cdot 1$ . The data regarding the specific heat of beryllium have been presented in Chapter I. par. 28, and it has there been shewn that, so far as specific heat data are concerned, the atomic weight of this element is probably represented by the number 9.1. The specific heat of beryllium, we found, increases rapidly as temperature rises, and in this respect shews an analogy with the specific heats of boron, carbon and silicon. If the mean values of the specific heats for the temperature-interval  $0^\circ$  to  $100^\circ$  of the metals in series 2 and 3 are multiplied into the atomic weights of these metals, it is found that the atomic heat decreases as the fusibilities of these metals decrease and as the atomic weights increase; thus,

## Atomic heat.

Li, 6.6
Be, 3.8 [if Be = 9.1]
B, 2.6
C, 2.4

## Atomic heat.

Na, 6.7
Mg, 5.9
Al, 5.5
Si, 4.6

The value to be assigned to the atomic weight of beryllium cannot however be regarded as finally settled by the determinations already made of the specific heat of this metal.

Nilson and Pettersson<sup>1</sup> insist that the molecular heats and specific volumes of the oxide and sulphate of beryllium, and also the atomic heat of oxygen in this oxide, establish the formulæ of these bodies to be  $\text{Be}_2\text{O}_3$  and  $\text{Be}_2 \cdot 3\text{SO}_4$  respectively; and therefore, these chemists argue that the atomic weight of the metal is 13.65, and beryllium must be placed in the group which comprises aluminium, gallium, indium, &c. On the other hand, Brauner<sup>2</sup> gives data from which it would appear that the molecular volumes (i.e.  $\frac{\text{formula weight}}{\text{specific gravity}}$ ) of beryllium oxide and sulphate, assuming the formulæ  $\text{BeO}$  and  $\text{BeSO}_4$  as correct ( $\text{Be} = 9.1$ ), are what might be expected from the position of beryllium (9.1) in group II. series 2.

Brauner<sup>3</sup> gives in tabular form the data concerning the molecular heats (i.e. formula weight  $\times$  specific heat) of metallic oxides, arranging the metals in groups and series. These data shew that the value of the 'molecular heat'<sup>4</sup> of the oxides—calculated in each case for one atom of metal in the oxide—varies considerably: 'the oxides of the metals of a 'natural group have nearly the same molecular heats, but the 'value increases as the atomic weights of the metals increase.' If the atomic heat of the metal in each of these oxides is deducted from the molecular heat of the oxide—calculated as mentioned above—the remainder represents the 'atomic heat of oxygen in the oxide.'<sup>4</sup>

Brauner gives the following table.

<sup>1</sup> *Ber.* 13. 1459.

<sup>2</sup> *Ber.* 14. 53.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> These expressions must be taken as meaning, in one case, the product (formula weight  $\times$  spec. heat), and in the other, (formula weight of oxide  $\times$  spec. heat) - (atomic weight of metal in oxide  $\times$  spec. heat).

'Atomic heat of oxygen in metallic oxides.' (BRAUNER.)

	GROUPS					
	I	II	III	IV	V	VI
Series						
2		Be, 2'4	B, 2'6			
3		Mg, 3'8	Al, 2'6	Si, 2'8		
4		Ca, 3'4	Sc, 2'7	Ti, 3'8		
5	Cu, 4'6	Zn, 3'9	Ga, 2'9			
6			Y, 3'5	Zr, 3'6		Mo, 4'1
7			In, 3'1	Sn, 3'8		
8			La, 4'0	Ce, 4'4	Di, 4'9	
9						
10			Yb, 4'2			W, 4'1
11		Hg, 4'8				
12				Th, 4'0		

The atomic heat of oxygen in the oxides increases as the atomic weights of the metals in each group increase; the value of the atomic heat of oxygen in beryllium oxide is smaller than the value for any other oxide in the group; hence beryllium should come in group II, series 2.

Carnelley's determination of the melting-point of beryllium chloride (see *ante*, par. 108) points to the beginning of group II as the proper position for beryllium, and hence to the number 9'1 as the atomic weight of this metal.

The general chemical characters of beryllium salts are summed up in the three statements<sup>1</sup> (Be = 9'1):

- (1) Li : Be = Be : B
- (2) Li : Na = Be : Mg = B : Al
- (3) Li : Mg = Be : Al = B : Si.

<sup>1</sup> See Brauner, *Ber.* 14. 53.



Hence we may conclude that there is a large probability in favour of the value 9.1 for the atomic weight of beryllium. This conclusion is supported by Hartley's observations on the spectrum of beryllium and his comparison of that spectrum with those of metals in group II. and III<sup>1</sup>.

Nilson and Pettersson have very recently succeeded in gasifying beryllium chloride; their determination of the density of this compound in the state of gas shews that the formula  $\text{BeCl}_2$  ( $\text{Be} = 9.1$ ) really represents the molecular weight of the substance<sup>2</sup>.

The mean values for the atomic weights of the three metals, cerium, lanthanum, and didymium, deduced from the most trustworthy data are

	(1)	(2)	(3)
	If oxide = $\text{MO}$	: if oxide = $\text{M}_2\text{O}_3$	: if oxide = $\text{MO}_2$ .
La =	92.33	138.5	184.7
Ce =	94	141	188
Di =	96	144	192

Numbers somewhat smaller than the values in column (1) were formerly generally adopted. In the earlier work on these metals very varying results were obtained by different chemists. Mendelejeff proposed to multiply the generally accepted atomic weights of cerium and didymium by 1.5 and that of lanthanum by 2; he thus got the values  $\text{Ce}^3 = 139$ ;  $\text{Di} = 138$ ;  $\text{La} = 180$ . If this multiplication is performed on the more accurately determined values given in column (1) above, we have  $\text{Ce} = 141$ ;  $\text{Di} = 144$ ;  $\text{La} = 184.7$ .

Cerium forms two oxides,  $\text{CeO}$  and  $\text{Ce}_2\text{O}_3$  if  $\text{Ce} = 94$ ,  $\text{Ce}_2\text{O}_3$  and  $\text{CeO}_2$  if  $\text{Ce} = 141$ . Mendelejeff placed cerium in group IV, the general formula for the highest oxide characteristic of this group being  $\text{RO}_3$ ; lanthanum he placed in the same group but in the series next after that which contained cerium; didymium found a place in group III (oxide =  $\text{R}_2\text{O}_3$ ), coming after yttrium and indium and preceding erbium<sup>4</sup>.

<sup>1</sup> *C. S. Journal Trans.* for 1883. 316.

<sup>2</sup> *Ber.* 17. 987.

<sup>3</sup> In a note (see *Chem. News*, 41. 49, note) Mendelejeff gives distinct reasons for thinking that this number, although that deduced from the best experimental evidence then available, is too small.

<sup>4</sup> The atomic weight of erbium was not then determined with any accuracy.

The properties of cerium compounds were fairly well known at this time, and Mendelejeff's arguments were very strong<sup>1</sup>; the facts known concerning salts of lanthanum and didymium were however scanty, and Mendelejeff did not strongly press the arguments in favour of the new positions assigned them in his scheme of classification. More recent and trustworthy work has established the numbers in column (1) above as the equivalents of the three metals (the atomic weight of erbium has also been established as about = 166); hence the positions assigned by Mendelejeff to didymium and lanthanum must be altered. Cerium<sup>2</sup> remains in group IV ( $\text{RO}_2$ ), series 8. Didymium occupies a position in series 8 of group V; the oxide  $\text{Di}_2\text{O}_3$  and the oxychloride  $\text{DiOCl}$ , which ought to exist if this position is correct, have lately been obtained by Brauner<sup>3</sup>; ( $\text{Di}_2\text{O}_3$  is much more stable than  $\text{Bi}_2\text{O}_3$ , as would be expected from the position of didymium in the periodic arrangement). No place is however found for  $\text{La} = 184.7$ ; but if the equivalent of lanthanum ( $92.33$ ) is multiplied by  $1.5$ , then  $\text{La}$  ( $138.5$ ) will occupy a place also in series 8, but in group III ( $\text{R}_2\text{O}_3$ ), being preceded by indium and succeeded by an element, as yet unknown, with atomic weight about 160.

The numbers obtained by Hillebrand<sup>4</sup> for the specific heats of the three metals under consideration fully confirm the values assigned to the atomic weights of these metals by the application of the periodic law; thus,

	Spec. heat.	Atomic heat.
Ce	0.0448	4.2 if Ce = 94 6.3 „ = 141
La	0.0449	4.2 if La = 92.33 6.2 „ = 138.5 8.3 „ = 184.7
Di	0.0456	4.4 if Di = 96 6.6 „ = 144

<sup>1</sup> See *Chem. News*, 41. 49.

<sup>2</sup> This position for cerium is strengthened by Brauner's preparation of  $\text{CeF}_4 \cdot \text{H}_2\text{O}$  and  $2\text{CeF}_4 \cdot 3\text{KF} \cdot 2\text{H}_2\text{O}$ . (Brauner, *loc. cit.*)

<sup>3</sup> *C. S. Journal, Trans.* for 1882. 73.

<sup>4</sup> *Pogg. Ann.* 158. 71.

In the table on p. 225 iodine and tellurium are placed in series 7, but  $I > \text{Te}$ . The older determinations of the atomic weights of these elements made  $\text{Te} > I$ ; nor is this result contradicted by the recent work of Wills<sup>1</sup>. Nevertheless as the numbers obtained by Wills range from 126.07 to 128.0, we are, I think, justified in provisionally placing tellurium in group VI and iodine in group VII. To reverse the positions of these elements would be entirely to obscure the analogies of both with other elements<sup>2</sup>.

Uranium is another element the comparative study of the properties of which has been much advanced by the application of the periodic law. The atomic weight of this element has been established as  $=n \cdot 120$ . If  $n=1$ , the three oxides of uranium must be formulated  $\text{UO}$ ,  $\text{U}_2\text{O}_3$ , and  $\text{U}_3\text{O}_4$ ; but there is no place for an element with this atomic weight and forming these oxides in the periodic arrangement. If however  $n=2$ , then ( $U=240$ ) the oxides become  $\text{UO}_2$ ,  $\text{UO}_3$ , and  $\text{U}_2\text{O}_7$ , and uranium finds a place in VI—12. The preceding members of this group—Cr, Mo, W—yield oxides ( $\text{RO}_3$ ) which are acid-forming. But a comparative study of the relations between the properties of oxides and the atomic weights of the elements in these oxides shews, that as the atomic weights of the elements in a group increase, the acid character of the higher oxides formed by these elements becomes less marked (e.g.  $\text{CrO}_3$  is more markedly an acid oxide than  $\text{MoO}_3$  or  $\text{WO}_3$ ). Now the highest oxide of uranium is an acid-forming oxide, but its acid functions are less marked than those of  $\text{CrO}_3$ ,  $\text{MoO}_3$ , and  $\text{WO}_3$ ; salts corresponding to  $\text{K}_2\text{CrO}_4$  and  $\text{K}_2\text{Cr}_2\text{O}_7$ , in which Cr is replaced by U are known. Uranic chloride,  $\text{UCl}_4$  if  $U=240$ , resembles  $\text{MoCl}_4$  in being volatile and decomposable by water.

The atomic volume (i.e.  $\frac{\text{atomic weight}}{\text{spec. gravity}}$ ) of the four

<sup>1</sup> C. S. *Journal Trans.* for 1879. 704.

<sup>2</sup> Brauner has recently obtained values for the atomic weight of tellurium varying from 124.94 to 125.4 (mean = 125); he has shewn that the process employed by Wills gives too high results unless great precautions are taken. (See abstract in *Ber.* 18. 3055.)

metals, Cr, Mo, W, U, increases as atomic weight increases, the values being Cr = 7·6; Mo = 11; W = 11; U = 12·5.

Hence from the comparative study of uranium compounds guided by the periodic law, we appear to be justified in adopting 240 as the atomic weight of this metal.

Recent determinations of the densities of gaseous uranium bromide and chloride, and of the specific heat of pure uranium, have fully confirmed this number (see *ante*, Chap. I. pars. 19, and 25).

112. The facts enumerated in the preceding pages undoubtedly establish the periodic law on a firm basis, and justify the employment of this law as one of the main guides in a general scheme of chemical classification<sup>1</sup>.

The following arrangement of the elements (the table is taken, with a few alterations, from a paper by Mendelejeff in *Ber.* 13. 1804) is in the opinion of Mendelejeff himself the best for clearly setting forth the general teaching of the periodic law. (See next page.)

Each group—except group VIII—contains members belonging to odd and to even series; or it may be said that each vertical column, or large series, is subdivided into two parts having seven elements in each. The entire column, comprising an odd and an even series, forms a 'long period'; the seven members in the even or in the odd series form a 'short period.' The members of group VIII form 'transition periods' from series 4 to 5, 6 to 7 (probably 8 to 9), and 10 to 11. Including the 'transition periods,' each 'long period' theoretically contains 17 elements.

Because of its peculiar properties, and also because of the anomalous relations between the values of its atomic weight and those of succeeding elements, hydrogen is regarded as the sole representative of group I, series 1.

Comparing series, we find closer analogies between corresponding members of odd or of even series, than between those of odd and even series: thus, comparing series 4 and 6,

<sup>1</sup> It is very unfortunate that Mendelejeff's *Treatise on Chemistry*, in which, as I understand, this law is made the basis of a general system, should not be published in some one of the languages of Western Europe.



and 4 and 7, potassium and rubidium are seen to be more closely related than potassium and silver; calcium and strontium, than calcium and cadmium; vanadium and niobium, than vanadium and antimony. Again, comparing series 5 and 7, and also 5 and 6, it is seen that the relations between zinc and cadmium, or between arsenic and antimony, are closer than those between zinc and strontium, or arsenic and niobium.

Omitting the typical elements, it may be said that, as a rule, the most markedly nonmetallic elements are placed in odd series. Also, that the passage from an even to an odd series is accompanied by a gradual change, but that from an odd to an even series by a more sudden change in the properties of the elements; thus chromium and manganese resemble copper and zinc much more than selenium and bromine resemble rubidium and strontium, or than tellurium and iodine resemble caesium and barium. It may also be laid down as a general proposition that volatile organo-metallic compounds are formed only by metals which occur in odd series; should such compounds be hereafter formed containing metals which belong to even series, the properties of the compounds in question will probably differ much from those of the volatile organo-metallic compounds at present known. (Mendelejeff.)

The elements which form the 'transition periods' (group VIII) possess many characteristic properties. They are very infusible, have small atomic volumes, and occlude oxygen and other gases; oxides of the form  $RO_4$  are met with in this group only; the highest oxides are basic or very feebly acid; these metals form stable alkaline double cyanides  $K_4RCy_6$ ,  $K_2RCy_6$ , or  $K_3RCy_6$ , and also stable ammoniacal compounds<sup>1</sup>.

The elements in series 2 (from lithium to fluorine), and perhaps the first member of series 3, viz. sodium, are grouped together as 'typical' elements. There is no 'transition period' coming between the even series 2 and the odd

<sup>1</sup> See Mendelejeff, *Chem. News*, 40. 267.

series 3 as there is between series 4 and 5, 6 and 7, and 10 and 11. The mean difference between the atomic weights of two elements in successive even series and in the same group (e.g. between potassium and rubidium, or between rubidium and cæsium) is 45; but the mean difference between the atomic weight of an element in series 4 and the corresponding element (i.e. the element in the same group) in series 2 is 35: hence we should expect to find the relations of series 2 to other series different from the general mutual relations exhibited by these other series. As the lower members of an homologous series of carbon compounds are sometimes characterised by the possession of properties which do not belong to the higher members, so the elements with atomic weights ranging from 1 to 19 (? 23) are characterised by special properties; they are 'typical' elements.

113. As the atomic weight increases in each group, the basic character of the higher oxides formed by the members of the group becomes more marked, and at the same time these oxides become more easily reduced. It is also to be noted that the composition of the more stable haloid and oxyhaloid salts (and in some cases of the more stable salts as a whole) tends, as atomic weight increases, to correspond in form with an oxide containing less oxygen than the highest oxide. These statements hold good more especially for those members of a group which occupy the odd series. Group v presents a good example.  $\text{Sb}_2\text{O}_5$  is more basic than  $\text{P}_2\text{O}_5$ , and  $\text{Bi}_2\text{O}_5$  is marked by an almost complete absence of acid properties. The highest oxides of this group belong to the form  $\text{RX}_5$  (see p. 243); the stable haloid and oxyhaloid salts of phosphorus, vanadium, niobium ( $\text{PF}_5$ ,  $\text{VOCl}_5$ ,  $\text{NbCl}_5$ ), belong to the same form, but the bismuth haloid and oxyhaloid salts are  $\text{BiCl}_3$ ,  $\text{BiBr}_3$ ,  $\text{BiOCl}$ ,  $\text{BiOBr}$ , &c., which belong to the form  $\text{RX}_3$ , characteristic of the lower oxide  $\text{Bi}_2\text{O}_3$ .

The first and last members of a series, and more especially of a 'long period,' present marked differences in their general chemical behaviour; thus lithium, potassium, and rubidium, the first members of the long periods 1, 2, and 3, are strongly positive, whereas the last members of the same periods,

viz. chlorine, bromine, and iodine, are typically negative elements.

114. The form of the highest oxides, and of some of the other salts, appears to be a periodic function of the atomic weights of the elements. In dealing with this question it will be well to use the term 'formula weight' rather than molecular weight, as the molecular weights of very few oxides have been determined.

If  $R$  be used to represent the amount of an element expressed by its atomic weight, and  $X$  to represent the amounts of Cl, Br, I, F, expressed by the respective atomic weights of these elements, or the amounts of the groups (OH), (NO<sub>3</sub>), (ClO<sub>3</sub>), &c., expressed by these formulæ, or the amounts of the following elements or groups of elements expressed by *half* the formulæ, viz. O, S, (SO<sub>4</sub>), (CrO<sub>4</sub>), &c., then we may say that the oxides



belong respectively to the forms



also that the salts



belong respectively to the forms



It becomes possible to give general expressions for the forms of the highest stable oxides characteristic of each group; thus,

Group	I	II	III	IV	V	VI	VII	VIII
	$R_1O$	$R_2O_2$	$R_3O_3$	$R_4O_4$	$R_5O_5$	$R_6O_6$	$(R_7O_7)$	$(R_8O_8)$
or	$RX$	$RX_2$	$RX_3$	$RX_4$	$RX_5$	$RX_6$	$(RX_7)$	$(RX_8)$

This statement may be put thus; the number of oxygen atoms in the general expression for the highest stable oxide characteristic of each member of a series increases, as the atomic weights of the members of the series increase.

Most of the stable salts (haloid salts, oxyhaloid salts, nitrates, sulphates, chromates, phosphates, &c.) characteristic



of the members of each group belong to the same general form ( $RX$ ,  $RX_2$ , &c.) as the oxides. But in every group well-marked salts are known which belong to higher forms than the oxide form: thus, some of the members of group I form peroxides ( $K_2O_2$ ,  $K_2O_4$ , &c.); some of the elements in group II form salts (such as  $K_2BeF_4$ ,  $K_2ZnCl_4$ , &c.) of the form  $RX_6$ ; salts, such as  $BOCl_3$ ,  $KBF_4$ ,  $KAlBr_4$ , &c., belonging to the form  $RX_5$ , are found in group III. The forms of the highest salts belonging to each group, and also the oxide forms, are given by Brauner<sup>1</sup>; thus,—

Groups,	I	II	III	IV	V	VI	VII	VIII
Salt forms,	$RX_7$	$RX_6$	$RX_5$	$RX_4$	$RX_3$	$RX_2$	$RX$	$(R_2X)$
Oxide forms,	$R_2O$	$R_2O_2$	$R_2O_3$	$R_2O_4$	$R_2O_5$	$R_2O_6$	$(R_2O_7)$	$(R_2O_8)$

or thus—

Salt forms,	$RX_7$	$RX_6$	$RX_5$	$RX_4$	$RX_3$	$RX_2$	$RX$	$(R_2X)$
Oxide forms,	$RX$	$RX_2$	$RX_3$	$RX_4$	$RX_5$	$RX_6$	$(RX_7)$	$(RX_8)$

The statements generalised in these expressions can be accepted only as rough approximations to general truths. Oxides of the forms given in the table are sometimes less stable than oxides of other forms—e.g.  $CuO$  is more stable than  $Cu_2O$ ,  $PbO$  than  $PbO_2$ , &c.; the form chosen for the highest oxides is sometimes scarcely known to be represented by actually occurring compounds,—thus the form  $R_2O_7$ , characteristic of group VII, finds its only representative in  $I_2O_7$ , and the existence of this oxide cannot be regarded as proved. Again, salts belonging to the general expressions given as representing the highest forms are sometimes fairly characteristic of the group, in other cases it is only by a dexterous manipulation of formulæ that the existence of such salts can be discovered; thus a great many well-marked salts of the members of group V undoubtedly belong to the form  $RX_3$ , but it is only by having recourse to such a substance as  $NaOH.3H_2O$  that a salt of the form  $RX_7$  can be found belonging to group I.

<sup>1</sup> *Sitzberichte der K. Akad. zu Wien, (math-naturwiss. classe)* 84. 1165.

Relations can be traced between the general forms of hydrogen and hydroxyl compounds, especially in groups IV, V, VI, and VII; thus,—

Group,	IV	V	VI	VII
Hydrogen compounds,	$RH_4$	$RH_3$	$RH_2$	$RH$
<i>e.g.</i>	$SiH_4$	$PH_3$	$SH_2$	$ClH$
Hydroxyl compounds,	$RH_4O_4$	$RH_3O_4$	$RH_2O_4$	$RHO_4$
<i>e.g.</i>	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	$ClO_3(OH)$

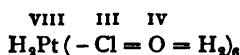
Dalton, and after him Berzelius, sought to elucidate the laws of atomic synthesis; they strove to find forms capable of expressing the maximum number of atoms of this or that element which could combine to form salts. But much had to be done before these limiting forms could be found: a firm standing ground appears to be now gained in the periodic law; to build a structure worthy of the foundation must be the work of the future.

115. The valency of the elementary atoms probably varies periodically with the relative weights of these atoms. Thus taking series 2, and assuming that the atom of lithium is monovalent and that of beryllium divalent, it is seen that in this series the valency of the elementary atoms increases from one to four, and again diminishes from four to one;

	Li	Be	B	C	N	O	F
Valency,	1	2	3	4	3	2	1.

If the evidence were sufficient to warrant the assumption that the valency varies in every series in the same way as in series 2, we should have in the periodic law a most important aid towards determining the valencies of all the elementary atoms. But the evidence at present available concerning valency does not permit us to make this assumption. A probable value for the valency of an elementary atom may be deduced from the position of the element in the periodic arrangement, but this value must not be considered as final. It has indeed been sought to fix the valencies of elementary atoms from considerations drawn from the positions of these elements in the periodic classification; but this has been done only by attaching to the term 'valency' a much looser

meaning than that which I have attempted to shew must be given if an exact theory is to be developed. In applying the periodic law to determine the valencies of elementary atoms, the formulæ of oxides and of solid salts generally have been employed as data from which conclusions might be drawn. But if we define the valency of an atom as the maximum number of other atoms with which the given atom can combine to form a molecule, then, to deduce valencies from a study of solid salts we must assume, (1) that the formula of a solid salt certainly represents at least the proportion between the numbers of atoms of each element in the molecule; (2) that the atom, the valency of which is to be determined, acts on, and is acted on by, certain other atoms in the molecule—in some cases it may be action is assumed between all the atoms, in other cases only between some of the atoms, in the molecule; and (3) we must assume a value for the valency of each atom, other than the given atom, in the molecule. Thus, to take an extreme case hydrated chloroplatinic acid,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ , has been represented thus—



in order that the platinum atom may be represented as octo-valent.

I have already<sup>1</sup> discussed assumptions (2) and (3), and have, I hope, shewn how vague and unsatisfactory any theory of valency must be which in the present state of knowledge is based on the study of other than gaseous compounds. A solid compound is prepared with definite properties; analysis serves to fix the composition; the atomic weights of the elements in the compound being known, a formula is found:—but to assume that this formula necessarily represents the ratio between the numbers of different elementary *atoms* in the *molecule* of this compound, is I think more than a fair inference from the facts. For is not this to assume that the ‘chemical unit’ of the solid compound is *a* molecule, whereas it may

<sup>1</sup> See chapter II. section 3, par. 63.

very possibly be a group of molecules? The definition of 'molecule' is a physical definition, and is strictly applicable only to gaseous bodies. The properties of a solid may be the properties of a number of little definite parts, each of which decomposes into two or more simpler groups (molecules) when the solid is gasified; the ratio between the numbers of atoms in the true molecules may be different from the ratio between the numbers of atoms in those groups of molecules, which form the building-stones of the solid compound.

But it may be urged that a much wider meaning ought to be given to the term valency. Better, I would reply, employ another term, or terms. Let us build as far as we can on the theory of valency; so far as it goes it is definite, without it the chemistry of carbon compounds especially could not have made the advances which it has made. But it is not all. The periodic law emphasises the existence of typical forms for the compounds of elements; it points to limiting values for the numbers of atoms which can be associated together in groups. It teaches the importance, in the chemistry of solid and liquid compounds, of the law of multiple proportions. It reminds us that at present we must study the properties of groups of compounds, that we must sum up these properties in the simplest possible formulæ, and that the whole chemical history of each compound must determine the form to be given to the symbol by which we express that history. It tells us that, although we do not know whether such formulæ do or do not represent the relative weights of the molecules of the bodies formulated, nevertheless these formulæ can be classified under a few types; and that thus a certain amount of order can be introduced into the classification of solid and liquid compounds, general conclusions can be drawn, and predictions can be made which may be submitted to the test of experiment. And while doing this, the periodic law keeps before us the necessity of from time to time modifying our scheme of classification; it reminds us that a typical classification is of necessity temporary, but that just by reason of its elasticity it

is suited to the present needs of the chemistry of solid and liquid substances<sup>1</sup>.

<sup>1</sup> It is interesting to observe in the applications of the periodic law the survival, in modified and more precise form, of the old conception of the element as an essence or principle, capable of impressing on all substances into which it entered properties sufficiently definite to mark off these substances from all others which did not contain this principle.

An interesting and important paper on the periodic law, especially as applied to the classification of elements and compounds, by T. Bayley, will be found in *Phil. Mag.* (5) 13. 26.

An important paper has just appeared by Carnelley (*Phil. Mag.* for July, 1884), in which the periodic law is illustrated by considering the melting and boiling points, and to some extent also the heats of formation, of the halogen compounds of the elements; and the facts thus obtained are applied to determine the values to be assigned to the atomic weights of various elements, and also the positions of these elements in the general scheme of classification based on the law in question. The case of beryllium is considered in detail in this paper.

## CHAPTER IV.

APPLICATION OF PHYSICAL METHODS TO QUESTIONS OF  
CHEMICAL STATICS.

116. CHEMISTRY being a more concrete science than physics must of necessity derive help in solving its problems from the use of physical methods of investigation: but while using such methods the chemist ought not to forget that his aim is to find answers to chemical, not to physical questions.

Minute descriptions of physical processes, and details of physical experiments are not demanded in a treatise on physical chemistry; much less is there required elaborate enunciations of the methods of calculation employed in physical researches. Such things give it is true an appearance of great accuracy and profound knowledge; but the apparently accurate knowledge and full discussion of physical details too frequently serves as an excuse for loose statements and superficial generalisations regarding those vital chemical questions for answering which so vast a collection of 'precautionary and vehiculatory gear' has been provided. In attempting to give an outline of the more important applications of physical methods to chemistry one is also liable to err in the other direction: vague statements to the effect that the boiling points of homologous hydrocarbons exhibit constant differences, or that the molecular structure of carbon compounds is intimately connected with their optical activity, or that chemical actions which involve a loss of energy in the reacting systems frequently occur,—statements such as these are utterly inadequate.

I cannot hope to avoid both dangers: but I may venture to believe that the contents of the present chapter will be of some assistance to those who attempt to gain clear conceptions on the important phenomena forming the subject-matter of physical chemistry.

Of the physical methods employed by the chemist as aids in attempts to solve the questions of chemical statics, I shall consider (1) thermal methods, (2) optical methods, (3) methods which involve measurements of the volumes of reacting substances, and (4) methods based on determinations of 'etherification-values'.

### SECTION I. *Thermal Methods*<sup>1</sup>.

117. The principle of the conservation of energy lies at the root of all thermo-chemical investigation. When two or more chemical substances react so as to produce a new system, or new systems of substances, mechanical work may be done by expansion, electrical currents may be produced, heat may be generated, and energy may be lost in the forms of sound or radiant heat. The sum of these various kinds of energy, together with the energy remaining in the final system, must be equal to the energy which was present in the original system. A very large part of the energy lost during chemical changes generally leaves the changing systems in the form of heat; hence, measurements of the quantities of heat evolved during definite chemical processes afford valuable information with respect to the differences between the amounts of energy possessed by the systems in their original and final states. To measure such differences of energy is the primary aim of thermal chemistry.

<sup>1</sup> Principal text-books on the subject are NAUMANN's *Lehr- und Handbuch der Thermochemie* (1882). THOMSEN's *Thermochemische Untersuchungen*, containing in a systematic form the work of many years which has hitherto been scattered through various memoirs: 3 vols. are now (1884) published. BERTHELOT's *Essai de Mécanique Chimique fondée sur la Thermochimie*, 2 vols. (1879) with supplement. JAHN'S *Die Grundsätze der Thermochemie* (1882).

We are accustomed to conceive of most chemical changes as divisible broadly into two parts, (1) separation of molecules into atoms, (2) re-arrangement of atoms to form new molecules. We picture to ourselves the final arrangement of the atoms as dependent on the nature of these atoms, and on their relative positions in the molecules which composed the original system, that is to say, we picture the progress of mutual actions and reactions among the separated atoms. As we know little, or nothing, of the causes of this re-arrangement, we are accustomed to say that 'the atoms are attracted towards each other by the force of chemical affinity'.

Consideration of the circumstances under which chemical changes proceed will, I think, make it evident that measurements of the quantities of heat evolved during these changes do not represent measurements of the 'chemical affinities'<sup>1</sup> of the reacting atoms; but these measurements do enable us to draw conclusions as to the constitution of chemical substances, and the general laws of chemical change.

The bearing of thermochemical measurements on the subject of affinity and chemical equilibrium in general will be considered in the second book: in the present section I propose to give a sketch of the methods of thermal chemistry, and a summary of the more important results obtained relating to allotropy, isomerism, nascent state, and other phenomena of chemical statics.

118. The notation of thermal chemistry is very simple: the formulæ of the reacting substances are enclosed in a square bracket, and each formula is separated from the other by a comma. Thomsen writes the figure expressing the number of atoms of each element above the symbol of that element.

Thus, the formula  $[H^2, Cl^2] = 44,000 +$ , means that a quantity of heat sufficient to raise the temperature of 44,000 grams of water from  $0^\circ$  to  $1^\circ C.$ , is evolved during the chemical process represented in ordinary notation by  $H_2 + Cl_2 = 2HCl$ , the quantities of hydrogen and chlorine being taken in grams<sup>2</sup>.

<sup>1</sup> See *post*, book II. chap. III.

<sup>2</sup> The unit of heat employed in this section is always to be taken as the gram-unit.



The symbol Aq, separated by a comma from another symbol, means that a large excess of water is present and that its effect in the total thermal change is taken into account; thus,  $[\text{HCl}, \text{Aq}] = 17,320 +$ , means that in the absorption of 36.5 grams of hydrochloric acid by an unlimited amount of water, 17,320 gram-units of heat are evolved;  $[\text{H}^2, \text{Cl}^2, \text{Aq}] = 61,320 +$ , means that the combination of 2 grams of hydrogen with 71 grams of chlorine in the presence of an unlimited amount of water is attended with the evolution of 61,320 gram-units of heat.  $[\text{HClAq}, \text{KOH Aq}] = 13,750 +$ , means that when 36.5 grams of HCl dissolved in a large excess of water react on 56 grams of KOH, also dissolved in a large excess of water, 13,750 gram-units of heat are evolved.

The symbol  $\text{H}^2\text{O}$  is used as in ordinary notation to represent 18 grams of water; thus

$$(1) [\text{Mn}, \text{O}^2, \text{SO}^2, 4\text{H}^2\text{O}] = 190,810 +;$$

$$(2) [\text{MnSO}_4\text{H}^2\text{O}, \text{Aq}] = 1770 +;$$

mean, (1) that in the formation of the amount, in grams, of crystallised manganous sulphate expressed by the formula  $\text{MnSO}_4\text{H}_2\text{O}$ , from the amounts, in grams, of manganese, oxygen, sulphur dioxide, and water, expressed by the respective formulæ  $\text{Mn}$ ,  $\text{O}_2$ ,  $\text{SO}_2$ , and  $4\text{H}_2\text{O}$ , 190,810 gram-units of heat are evolved: (2) that in the solution of the foregoing number of grams of crystallised manganous sulphate in an unlimited quantity of water 1770 gram-units of heat are evolved.

An ordinary chemical equation may be supplemented by the corresponding thermal symbol. Thus



i.e. 2 grams of hydrogen combine with 71 grams of chlorine to give 73 grams of hydrochloric acid, and the change is attended with the evolution of a definite amount of heat. The fact that the decomposition of  $2\text{HCl}$  into  $\text{H}_2$  and  $\text{Cl}_2$  is attended with the absorption of the same quantity of heat as is evolved during the union of  $\text{H}_2$  with  $\text{Cl}_2$  may be expressed thus



<sup>1</sup> This notation is however confused and awkward, and is scarcely used.

Generally then<sup>1</sup>, let  $r$  = the thermal value of a chemical change: let the change be the formation of a definite amount of a compound<sup>2</sup> (viz.  $X_aY_bZ_c$ ), consisting of  $a$  parts by weight of the element  $X$ ,  $b$  parts by weight of the element  $Y$ , and  $c$  parts by weight of the element  $Z$ ; then

$$r = [X^a, Y^b, Z^c] \dots\dots\dots(1).$$

Let the compound  $X_aY_bZ_c$  be produced as before, but in presence of a large excess of water which holds it in solution, then

$$r = [X^a, Y^b, Z^c, \text{Aq}] \dots\dots\dots(2).$$

Let the substance  $X_aY_bZ_c$  already existing be dissolved in an unlimited amount of water, then

$$r = [X^aY^bZ^c, \text{Aq}] \dots\dots\dots(3).$$

Let the compound  $XY$  be decomposed by the element  $Z$  with formation of  $XZ$  and  $Y$ , we get the expression

$$r = [XY, Z] = [X, Z] - [X, Y] \dots\dots\dots(4),$$

that is, the total thermal change consists of two parts, (a) the heat absorbed in separating  $XY$  into  $X + Y$ , and (b) the heat evolved in the union of  $X$  and  $Z$  to form  $XZ$ .

Finally let the compound  $XY$  react on the compound  $ZV$  to produce  $XZ$  and  $YV$ , the value of  $r$  is found by the formula

$$r = [X, Z] + [Y, V] - [X, Y] - [Z, V] \dots\dots\dots(5).$$

Equations (1) to (3) have been already illustrated. As an example of the use of (4) we may take the action of zinc on hydrochloric acid whereby zinc chloride and hydrogen are produced;



or that of iron on a solution of copper sulphate to produce ferrous sulphate and copper;



<sup>1</sup> Thomsen, *Thermochemische Untersuchungen*, 1. 5 et seq.

<sup>2</sup> In many cases we may use the term 'molecule' in place of 'definite amount', and 'atom' in place of 'parts by weight': but as we shall frequently deal with solids and liquids it is better at present not to speak of atoms and molecules.

As an illustration of (5) the decomposition of  $\text{PbO}$  by  $\text{H}_2\text{S}$  resulting in production of  $\text{PbS}$  and  $\text{H}_2\text{O}$ , may be used ;



119. A distinction is generally drawn between so-called exothermic and endothermic changes; the former are accompanied by evolution, the latter by absorption of heat.

Let  $(P^a Q^b)$  represent the energy in a compound formed of  $a$  parts of element  $P$  and  $b$  parts of element  $Q$ : let  $(P^a)$  and  $(Q^b)$  represent the energy in  $a$  parts of  $P$ , and in  $b$  parts of  $Q$  respectively; then, inasmuch as the energy in any system resulting from a definite chemical change is equal to the difference between the energy in the original system from which it was produced and that lost during the process, it follows that

$$(P^a Q^b) = (P^a) + (Q^b) - (P^a, Q^b),$$

assuming that the heat evolved in the formation of  $P^a Q^b$  measures the total loss of energy.

And  $\therefore (P^a) + (Q^b) > (P^a, Q^b).$

This equation represents an exothermic change.

But in some cases a chemical change occurs only when heat is added to the changing system from without; in such a case

$$(P^a Q^b) = (P^a) + (Q^b) + (P^a, Q^b),$$

and  $\therefore (P^a) + (Q^b) < (P^a Q^b).$

This equation represents an endothermic change.

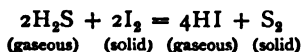
It has been stated that if an exothermic change is possible it will always occur. When we have advanced somewhat in our study of thermal chemistry we shall see how impossible it is to found a system of classification on the difference between exothermic and endothermic changes. In some cases, a chemical reaction which appears to be accompanied by

<sup>1</sup> Thomsen appears to be the only chemist who systematically writes the indices above the symbols of elements in the formulæ of thermal chemistry. Thomsen also sometimes uses the colon in place of the comma to express chemical reaction between the substances whose formulæ are separated by this symbol.

absorption of heat is found, on more careful study, to form one member of a series of changes the thermal sum of which is represented by a positive quantity. Indeed any chemical reaction is a most complex phenomenon when regarded from the thermal point of view; physical changes (expansion or contraction, passage from solid to liquid or gas, or *vice versa*, &c., &c.) form part of the total change, the thermal value of which is set down in a lump sum. But thermal chemistry aims at something more than this rough grouping together of positive and negative values. Thermal chemistry tries to disentangle the primary chemical, from the subordinate physical changes, and moreover to divide the chemical processes into those which consist of molecular decompositions, and those which consist of atomic combinations.

It is not possible to enter on any full discussion of the terms exothermic and endothermic as applied to chemical phenomena until the subject of affinity has been treated; at present I wish to insist on the inadvisability of making the conception implied in these terms the basis of a system of classification of chemical reactions, and at the same time to draw attention to some processes which are suggested by the terms in question.

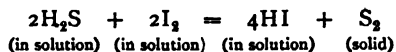
Naumann<sup>1</sup> shewed that no action occurs when dry sulphuretted hydrogen is passed into a solution of iodine in dry carbon disulphide, but that as soon as water is added, hydriodic acid and sulphur are produced. The reaction



would be thermally represented as

$$\begin{aligned} [2\text{H}^2\text{S}, 2\text{I}^2] &= 4[\text{H}, \text{I}] - 2[\text{H}^2, \text{S}] \\ &= -24800 - 9200 \\ &= -34,000. \end{aligned}$$

When water is present, the reaction



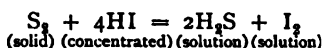
<sup>1</sup> Ber. 2. 177; and *Annalen* 151. 145.

would be thermally represented as

$$\begin{aligned}[2\text{H}^2\text{SAq}, 2\text{I}^2\text{Aq}] &= 4[\text{H}, \text{I}, \text{Aq}] - 2[\text{H}^2, \text{S}, \text{Aq}] \\ &= 52,800 - 18,400 \\ &= 34,400^1 +.\end{aligned}$$

The reaction of dry sulphuretted hydrogen on dry iodine would be markedly endothermic; but when this change is made one of a series the thermal value of which, taken as a whole, is positive, then the complete cycle of change proceeds rapidly.

But the more concentrated an aqueous solution of hydriodic acid becomes the less heat is there evolved on each addition of the acid, until the specific gravity of the liquid is 1.56<sup>2</sup>, after which no more heat is evolved; the liquid is saturated. If therefore the hydriodic acid produced in the foregoing reaction is allowed to accumulate in the liquid, no more water being added, a point will be reached at which the sum of the thermal changes is equal to zero; at this point the chemical change stops, but proceeds again on the addition of a little water. It is possible to obtain an aqueous solution of hydriodic acid of specific gravity 1.67; if sulphur is shaken with this liquid a little sulphuretted hydrogen and iodine are produced, i.e. the change



proceeds until the hydriodic acid becomes reduced to specific gravity 1.56, when equilibrium is again established.

Portions of this cycle of change are exothermic, other portions are endothermic. Variation of the mass of one of the members of the changing system determines whether the thermal value of the complete change shall be positive or negative, and also determines the direction in which the change shall proceed. This reaction may be taken as typical of most if not all chemical processes. Such processes consist of portions having positive thermal values and portions having negative values; small variations in the conditions may

<sup>1</sup> No notice is taken in these thermal expressions of the change, if any, which accompanies the decomposition of 2I<sub>2</sub> and the production of S<sub>2</sub>. See *post*, par. 132.

<sup>2</sup> This liquid contains about 25 per cent. of HI.

determine whether the process as a whole shall belong to the class of exothermic or to that of endothermic changes.

120. Direct measurements of the thermal changes which accompany chemical changes can only be made in a few simple cases; it is generally necessary to have recourse to indirect methods. The truth of the following deduction from the theory of energy is assumed in all these methods of calculation.

The total loss of energy by a chemical system in passing from a definite initial to a definite final state is independent of the intermediate states.

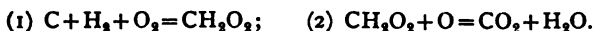
The total loss of energy is of course measured by the heat evolved and the work done by the system in its passage from one state to the other. But for our purpose the energy given out in forms other than that of heat may be overlooked, and we may put the statement in this form; the total thermal change during a chemical process is dependent only on the initial and final states of the chemical system.

In applying this statement, it is necessary to arrange series of reactions each beginning with the same materials in the same conditions and ending with the same products under the same conditions; all the processes which form one of the cycles of change must be capable of calorimetric measurement, and all the processes in the other cycle, except that one the thermal value of which is to be determined, must also be capable of measurement by the calorimeter: if this be done, it follows from the principle just stated that the difference between the total thermal values of the two cycles of changes represents the thermal value of that special portion of one of the cycles which it is wished to determine. Each cycle may however consist of various parts, so that it is sometimes a little difficult to unravel all the changes, and to find that portion of one cycle the thermal value of which has to be determined by calculation.

I shall now give some examples to shew how the thermal values of various chemical changes are deduced from the results of experiments.

A. It is required to determine the thermal value of the synthesis of  $\text{CH}_3\text{O}_2$  from C,  $\text{H}_2$ , and  $\text{O}_2$ .

We start with 12 grams of carbon, 2 of hydrogen, and 48 of oxygen; these combine to form 18 grams of water, and 44 grams of carbon dioxide ( $\text{C} + \text{H}_2 + \text{O}_2 = \text{CO}_2 + \text{H}_2\text{O}$ ). But the same quantities of carbon, hydrogen, and oxygen might be (theoretically) combined to form 46 grams of formic acid, which could then be oxidised, by 16 grams of oxygen, to form 18 grams of water and 44 grams of carbon dioxide. Stated in formulæ these changes are



The following are the thermal values of the different portions of these changes :

$$\begin{aligned} [\text{C}, \text{O}^2] &= 96,960 + : [\text{H}^2, \text{O}] = 68,360 + : [\text{CH}_3\text{O}^2, \text{O}] = 65,900 + \\ \text{but} \quad [\text{C}, \text{O}^2] + [\text{H}^2, \text{O}] &= [\text{C}, \text{H}^2, \text{O}^2] + [\text{CH}_3\text{O}^2, \text{O}] = 165,320 + \\ \therefore [\text{C}, \text{H}^2, \text{O}^2] &= [\text{C}, \text{O}^2] + [\text{H}^2, \text{O}] - [\text{CH}_3\text{O}^2, \text{O}] = 99,420 +. \end{aligned}$$

B. A rather more complicated example is furnished by the determination of the thermal values of the actions (1)  $[\text{H}, \text{Br}]$ , (2)  $[\text{H}, \text{I}]$ ; i.e. of the reactions whereby  $\text{HBr}$  and  $\text{HI}$  are conceived to be formed from their elements.

(1)  $[\text{H}, \text{Br}]$ . The data are

$$[\text{H}, \text{Cl}, \text{Aq}] = 39,300; \quad [\text{HBr}, \text{Aq}] = 19,900^1;$$

therefore assuming that

$$[\text{H}, \text{Br}, \text{Aq}] = [\text{H}, \text{Cl}, \text{Aq}]$$

it follows that

$$[\text{H}, \text{Br}] = 39,300 - 19,900 = 19,400.$$

But is the formation of an aqueous solution of  $\text{HBr}$  from  $\text{H}$ ,  $\text{Br}$ , and water attended with the same thermal change as accompanies the formation of an aqueous solution of  $\text{HCl}$  from  $\text{H}$ ,  $\text{Cl}$ , and water? Or, if this assumption is not justified by facts, what is the difference between the thermal values of the two changes?

Now, in the first place, the thermal values of the formation of  $\text{KCl}$  and  $\text{KBr}$  in aqueous solution are equal, i.e.

$$[\text{KOHAq}, \text{HClAq}] = [\text{KOHAq}, \text{HBrAq}].$$

<sup>1</sup> When no + or - sign is given it is to be understood that heat is evolved.

But the replacement of Br by Cl is attended with a considerable evolution of heat ; the data here are

$$[\text{KBrAq}, \text{Cl}] = 11,500.$$

Now if we analyse this change we find that the thermal expression when expanded becomes

$$[\text{K}, \text{Cl}, \text{Aq}] + [\text{Br}, \text{Aq}] - [\text{K}, \text{Br}, \text{Aq}] = 11,500:$$

but  $[\text{Br}, \text{Aq}] = 500:$

$$\therefore [\text{K}, \text{Cl}, \text{Aq}] - [\text{K}, \text{Br}, \text{Aq}] = 11,500 - 500 = 11,000.$$

That is to say, the replacement of Br by Cl in aqueous solution is represented by the thermal value 11,000 units, and as the heat of neutralisation, in aqueous solution, of KOH by HCl is equal to that of KOH by HBr, it follows that

$$[\text{H}, \text{Br}, \text{Aq}] = [\text{H}, \text{Cl}, \text{Aq}] - 11,000 = 28,300:$$

and as  $[\text{HBr}, \text{Aq}] = 19,900$ , it follows that  $[\text{H}, \text{Br}] = 8,400$ .

(2)  $[\text{H}, \text{I}]$ . The data are

$$[\text{H}, \text{Cl}, \text{Aq}] = 39,300; [\text{HI}, \text{Aq}] = 19,200.$$

Now

$$[\text{KOHAq}, \text{HIAq}] = [\text{KOHAq}, \text{HClAq}] - 70:$$

also

$$[\text{KIAq}, \text{Cl}] = 26,200 \text{ (iodine separating as solid):}$$

$\therefore$  replacement of I by Cl is accompanied by evolution of  $26,200 - 70 = 26,130$  units:

$$\therefore [\text{H}, \text{I}, \text{Aq}] = [\text{H}, \text{Cl}, \text{Aq}] - 26,130 = 13,170:$$

and as  $[\text{HI}, \text{Aq}] = 19,200$

it follows that  $[\text{H}, \text{I}] = -6,030$ .

C. The heat of formation of  $\text{H}_2\text{SO}_4$  from its elements, i.e. the thermal value of the change  $[\text{H}^2, \text{S}, \text{O}^4]$ , has been calculated by Berthelot. Thus,

(a) oxidation of sulphurous acid in aqueous solution by chlorine;

$$[\text{H}^2\text{SO}^3\text{Aq}, \text{H}^2\text{O}, \text{Cl}^2] = 73,900:$$

this expression when expanded becomes,

$$73,900 = 2[\text{H}, \text{Cl}, \text{Aq}] + [\text{H}^2\text{SO}^3\text{Aq}, \text{O}] - [\text{H}^2\text{O}].$$



But  $2[\text{H}, \text{Cl}, \text{Aq}] = 78,600$  : and  $[\text{H}^2, \text{O}] = 68,400$  :

$$\therefore [\text{H}^2\text{SO}^3\text{Aq}, \text{O}] = 73,900 - (78,600 - 68,400) = 63,700 + \dots\dots\dots(1)$$

$$(\delta) [\text{SO}^2, \text{Aq}] = 7,700 :$$

but, assuming that when  $\text{SO}_2$  is dissolved in water the solution contains  $\text{H}_2\text{SO}_3$ , it follows that

$$[\text{SO}^2, \text{Aq}] = [\text{H}^2\text{O}, \text{SO}^2, \text{Aq}] :$$

$$\therefore \text{from (1)} [\text{SO}^2, \text{H}^2\text{O}, \text{O}, \text{Aq}] = 63,700 + 7,700 = 71,400 + \dots\dots(2)$$

$$(\epsilon) [\text{S}, \text{O}^2] = 69,000 :$$

$$\therefore \text{from (2)} [\text{S}, \text{O}^2, \text{O}, \text{H}^2\text{O}, \text{Aq}] = 71,400 + 69,000 = 141,300 + \dots(3)$$

$$(\delta) [\text{SO}^2, \text{Aq}] = 37,400 :$$

now, dividing (3) into two parts, we have

$$\text{part (a)} \dots [\text{S}, \text{O}^2, \text{O}] \text{ and part (b)} \dots [\text{SO}^2, \text{H}^2\text{O}, \text{Aq}] ;$$

but we know the value of part (b), and also the total value,

$$\therefore [\text{S}, \text{O}^2, \text{O}], \text{ i.e. } [\text{S}, \text{O}^3] = 141,300 - 37,400 = 103,900 \dots\dots(4)$$

$$(\epsilon) [\text{H}^2\text{SO}^4, \text{Aq}] = 17,000 :$$

Now we have the values,

$$(a) [\text{S}, \text{O}^3] = 103,900 : (\delta) [\text{SO}^2, \text{H}^2\text{O}] = ? : (\epsilon) [\text{H}^2\text{SO}^4, \text{Aq}] = 17,000 :$$

$$(\delta) + (\epsilon) = 37,400 ;$$

$$\therefore [\text{SO}^2, \text{H}^2\text{O}] = 20,400.$$

$$\text{But } [\text{S}, \text{O}^3] = 103,900 ; \therefore [\text{S}, \text{O}^3, \text{H}^2\text{O}] = 103,900 + 20,400 = 124,300 \dots\dots(5)$$

$$(\gamma) \text{ but } [\text{H}^2, \text{O}] = 68,400 :$$

$$\therefore \text{from (5)} [\text{S}, \text{O}^3, \text{O}, \text{H}^2, \text{O}] \text{ i.e. } [\text{S}, \text{O}^4, \text{H}^2] = 124,300 + 68,400 \\ = 192,700 +.$$

The calculation of so-called *heats of formation* are all based on the principle we are now discussing.

D. Thus, required the heat of formation of methane ( $\text{CH}_4$ ). We start with the two systems (1)  $\text{C} + \text{H}_2$ , (2)  $\text{CH}_4$ . Each is completely oxidised to the same final products, viz.  $\text{CO}_2 + 2\text{H}_2\text{O}$ ; the difference between the quantities of heat evolved in these two changes is called the heat of formation of  $\text{CH}_4$ . Thus,

$$[\text{C}, \text{O}^2] = 96,900 : 2[\text{H}^2, \text{O}] = 136,800 : \text{sum} = 233,700$$

$$\text{but } [\text{CH}_4, \text{O}^2] = 213,500$$

$$\therefore [\text{C}, \text{H}^4] = 20,200 +.$$

As it is important that a definite meaning should be attached to the expression 'heat of formation,' a few more examples are given.

E. Required the thermal value of the reaction  $[H, C, N]$ , that is, of the reaction whereby HCN may be conceived to be formed from its elements.

*Data;*  $[C, O^2] = 96,900$ ;  $\frac{1}{2}[H^2, O] = 34,200$ ; sum = 131,100 (N is incombustible)  
 but  $[CNH, \frac{5}{2}O] = 159,500$   
 $\therefore [C, N, H]^1 = 28,400 -$ .

F. Required the thermal value of the reaction  $[N^2, O]$ .

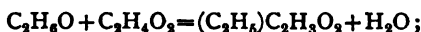
*Data;* the reaction

$C + 2N_2O = 2N_2 + CO_2$  when expanded thermally is  
 $[C, 2N^2O] = [C, O^2] - 2[N^2, O] = 133,900$ ;  
 but  $C + 2N_2 + O_2 = CO_2 + 2N_2$   
 i.e.  $[C, 2N^2, O_2] = [C, O_2] = 96,900$ ;  
 $\therefore 2[N^2, O] = 37,000 -$   
 $\therefore [N^2, O] = 18,500 -$ .

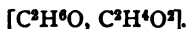
G. Required the thermal value of the reaction  $[N, O]$ .

*Data;*  $CN + 2NO = CO_2 + 3N$ , or in thermal notation  
 $[CN, 2NO] = [C, O^2] - [C, N] - 2[N, O] = 174,600$ ;  
 but  $CN + O_2 = CO_2 + N$   
 $= [C, O^2] - [C, N] = 130,900$ ;  
 $\therefore 2[N, O] = 43,700 -$   
 $\therefore [N, O] = 21,850 -$ .

H. Required the thermal value of the reaction



or in thermal notation



*Data;*  $[C^2H^6O, O^6] = 330,400$   
 $[C^2H^4O^2, O^4] = 210,300$  } sum = 540,700

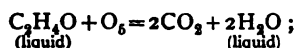
but  $[(C^2H^6)C^2H^3O^3, O^{10}] = 553,780$   
 $[H^2O, O] = 0$   
 $\therefore [C^2H^6O, C^2H^4O^2] = 13,080 -$ .

<sup>1</sup> The transference of N from the molecule  $N_2$  to the molecule HCN is assumed to be accompanied by no thermal change. See *post* par. 131.

The heat of formation of a substance will of course vary according as the substance is formed in the gaseous, liquid, or solid state, and also according to the temperature of formation. The following examples will illustrate this.

I. Required the thermal value of the formation of aldehyde from its elements, i.e. of the reaction  $[C^2, H^4, O]$ , when the aldehyde is (a) liquid, (b) gaseous.

(a) *Liquid: data,*



$$\begin{aligned} \text{i.e. } [C^2H^4O, O^6] &= 2[C, O^2] + 2[H^2, O] - [C^2, H^4, O] = 275,500 \\ &\text{but } 2[C, O^2] + 2[H^2, O] = 330,600 \end{aligned}$$

$$\therefore [C^2, H^4, O] \text{ liquid}^1 = 55,100 +.$$

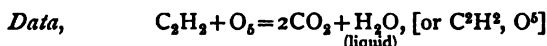
(b) *Gaseous: data,*

$$\underset{\text{(gaseous)}}{[C^2H^4O, O^6]} = 266,000; \text{ and } 2\underset{\text{(gaseous)}}{[H^2, O]} = 117,400:$$

$$\therefore [C^2, H^4, O] \text{ gaseous} = 45,200.$$

K. If the products of a reaction are gaseous and are maintained at a high temperature, it becomes necessary to introduce corrections for the specific heats, and heats of vaporisation, of these products, into the calculation of the thermal value of the reaction.

Thus, required the thermal value of the reaction  $[C^2H^2, O^3]$  at  $150^\circ$ .



at ordinary temperatures ( $20^\circ$ )  $= 2[C, O^2] + [H^2, O] - [C^2, H^2] = 310,600$  :  
but thermal capacity of 2 gram-molecules of  $CO_2$  for tem-  
perature-interval  $20^\circ - 150^\circ$  ... .. = 2482 units.

$$\begin{aligned} \text{thermal capacity of } \left\{ \begin{array}{l} (a) \text{ 1 mol. liquid } H_2O \text{ } 20^\circ - 100^\circ = 18.80 = 1440 \text{ ,,} \\ (b) \text{ heat of vaporisation of do. at } 100^\circ \\ \text{1 gram-molecule} \quad = 18.536 \cdot 5 = 9657 \text{ ,,} \\ \text{of } H_2O \quad (c) \text{ thermal capacity of 1 mol. steam} \\ \quad \quad \quad 100^\circ - 150^\circ = 18.50 \cdot 0 \cdot 4805 = 432 \text{ ,,} \end{array} \right. \\ \text{total} = 14011 \text{ units.} \end{aligned}$$

<sup>1</sup> The  $CO_2$  produced is gaseous; the heat of formation of liquid  $CO_2$  is unknown.

$\therefore [C^2H^2, O^5]$  at  $150^\circ = 310,600 - 14,011 = 296,589$  (say 296,600)  
gram-units.

The thermal values of reactions of various kinds may be determined by the use of the principle laid down in par. 120. The following are examples.

L. The heat of liquefaction of the hydrate  $H_2SO_4 \cdot H_2O$  is found to be  $-3680$  from these data,

$$[H^2SO^4H_2O, Aq] = 7120 : \quad [H^2SO^4H^2O, Aq] = 10,800.$$

(solid)  (liquid)

M. The mean thermal value of the fixation of each molecule of water by a salt when undergoing hydration may be found by using the formula  $\frac{L_o - L_n}{n}$ ;

where  $L_o$  = heat of solution of dehydrated salt,

$L_n$  = " " hydrated salt with  $n$  molecules of water.

thus, for  $Na_2SO_4$ ,

$$\begin{aligned} L_o &= 460 \text{ units} +. & L_n &= 1,900 \text{ units} -, \text{ when } n = 1: \\ & & &= 4,365 \text{ " } -, \text{ " } n = 2.4: \\ & & &= 10,100 \text{ " } -, \text{ " } n = 5.4: \\ & & &= 18,800 \text{ " } -, \text{ " } n = 10. \end{aligned}$$

Hence, calculating from the salt  $Na_2SO_4 \cdot 10H_2O$ , the mean thermal value of the reaction  $[Na^2SO^4, H^2O]$  is  $-1834$  units; and calculating from the salt  $Na_2SO_4 \cdot 5.4H_2O$ , the mean value for the same reaction is  $-1785$  units.

If the heat of liquefaction of water is subtracted from the difference  $L_o - L_n$ , we get the thermal value of the combination with solid water of the salt in question. Thus, taking sodium butyrate,

for  $C_4H_7NaO_2$ ;  $L_o = 4240$  units:

and for  $C_4H_7NaO_2 \cdot 3H_2O$ ;  $L_n = 3440$  " :  $\therefore L_o - L_n = 800$  units;

but heat of liquefaction of 3 gram-molecules water =  $-1430.3 = -4290$ :

$$\text{hence } \frac{800 - (-4290)}{3} = -1697:$$

i.e. the mean thermal value for the combination of each molecule of water, in the solid form, with  $C_4H_7NaO_2$  is represented by  $-1697$  gram-units.

N. The heat of formation in solution of a double salt, is the difference between the heat of solution of the double

salt, and the sum of the heats of solution of its constituents; thus,

Salts.	Heat of solution.	Sum (= A).	Double salts.	Heat of solution (= B).	Heat of formation, in solution, of double salt (B - A).
$K_2SO_4$	6340 -	- 8770	$K_2SO_4 \cdot CuSO_4 \cdot 7H_2O$	14360 -	5590 -
$CuSO_4 \cdot 5H_2O$	2430 -				
$(NH_4)_2SO_4$	1940 -	- 4370	$(NH_4)_2SO_4 \cdot CuSO_4 \cdot 7H_2O$	11240 -	6860 -
$CuSO_4 \cdot 5H_2O$	2430 -				

O. One other example of the calculation of a heat of formation will be given, as it serves to shew how very indirect are the methods sometimes adopted.

Required the thermal value of the reaction  $[Cl^2, O]$ .

*Data*, (1) for finding the value of  $[H, Cl, O, Aq]$ :

(a) the reaction  $2NaOH + Cl_2 = NaCl + NaClO + H_2O$ , if expanded thermally becomes

$$[2NaOH, Cl^2] = [H, Cl, Aq] + [H, Cl, O, Aq] - [H^2, O] \\ + [NaOHAq, HClAq] + [NaOHAq, HClOAq] = 24,600 :$$

but

$$[H, Cl, Aq] = 39,300$$

$$[H^2, O] = 68,400$$

$$[HClAq, NaOHAq] = 13,700$$

$$[HClOAq, NaOHAq] = 10,000 ;$$

$$\therefore 24,600 = [H, Cl, O, Aq] + 39,300 + 13,700 + 10,000 - 68,400 \\ [H, Cl, O, Aq] = 5,400 :$$

$$\therefore [H, Cl, O, Aq] = 30,000.$$

(b) the decomposition of aqueous  $HClO$  by aqueous  $HI$ , viz.  $2HI + HClO = HCl + H_2O + I_2$ , if expanded thermally becomes

$$[HClOAq, 2HIAq] = [H, Cl, Aq] + [H^2, O] - [H, Cl, O, Aq] \\ - 2[H, I, Aq] = 51,400 :$$

but

$$[H, Cl, Aq] = 39,300$$

$$[H^2, O] = 68,400$$

$$2[H, I, Aq] = 26,350 :$$

$$\therefore 51,400 = 81,350 - [H, Cl, O, Aq] :$$

$$\therefore [H, Cl, O, Aq] = 29,950.$$

Hence mean value of  $[H, Cl, O, Aq] = (29,975)$  say 30,000.

(2) Further data for finding  $[Cl^2, O]$ :

the reaction  $Cl_2O + H_2O = 2HClO$ , if expanded thermally becomes

$$[Cl^2O, H^2O] = 2[H, Cl, O, Aq] - [H^2, O] - [Cl^2, O] = 9400.$$

But we have already found

$$2[\text{H, Cl, O, Aq}] = 60,000 : \text{ and } [\text{H}^2, \text{O}] = 68,400 :$$

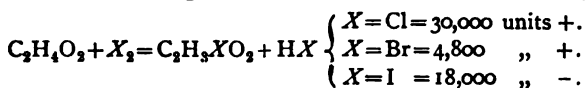
$$\therefore 9,400 = -8,400 - [\text{Cl}^2, \text{O}]$$

$$\therefore [\text{Cl}^2, \text{O}] = -17,800.$$

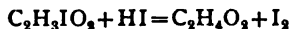
121. From these examples we may provisionally conclude that a chemical change which is accompanied by considerable loss of energy to the changing system will generally occur unless prevented by actions outside of the system.

The following processes may be taken as illustrative of this somewhat vague generalisation.

The acids of the acetic series readily yield chloro-, or bromo-derivatives by the direct action on them of chlorine or bromine, iodine however does not react under similar conditions to form iodo-acids. The thermal values of the reactions of the three halogens on acetic acid are as follows,



The reverse action in the case of iodine, viz.



is represented thermally thus,

$$[\text{C}_2\text{H}_3\text{IO}_2, \text{HI}] = 18,000.$$

This action occurs provided a concentrated aqueous solution of hydriodic acid is employed.

Now

$$\begin{aligned} 2\text{HI} &= \text{H}_2 + \text{I}_2, \\ (\text{gas}) & \quad (\text{solid}) \\ &= -2[\text{H}, \text{I}] \\ &= 12,400. \end{aligned}$$

But

$$[2\text{HI, Aq}] = 38,000 :$$

hence it follows that the decomposition of  $2\text{HI}$  into  $\text{H}_2 + \text{I}_2$ , in dilute solution would *absorb*  $38,000 - 12,400 = 25,600$  units of heat.

These thermal numbers shew that the process which is accompanied by a large loss of energy occurs, whereas that which would involve gain of energy to the system does not occur.

But why does a concentrated aqueous solution of hydriodic acid act as an energetic reducing agent? We have already

learned (par. 119) that little or no heat is evolved during the absorption and solution of gaseous hydriodic acid by a solution of that gas containing about 20—25 per cent. of HI; hence a concentrated solution of this compound contains a considerable quantity of HI, as distinguished from  $\text{HI} \cdot x\text{H}_2\text{O}$ . But the numbers given above shew that HI contains much more energy than  $\text{HI} \cdot x\text{H}_2\text{O}$ ; hence a concentrated aqueous solution of hydriodic acid is much more energetic than a dilute solution of the same compound<sup>1</sup>.

The following tables<sup>2</sup> contain thermal data for discussing the action of sulphuretted hydrogen as a reagent for precipitating certain metals from acid solutions, and other metals only from neutral or alkaline solutions.

TABLE I.

Reaction	Base						
	CdO	PbO	CuO	HgO	Tl <sub>2</sub> O	Cu <sub>2</sub> O	Ag <sub>2</sub> O
[Base 2HClAq, H <sup>+</sup> SAq] } (1)	27,300	29,200	31,700	45,300	38,500	38,500	58,500
[Base Aq, 2HClAq] } (2)	20,300	15,400	15,300	19,000	27,500	14,700	42,600
(1) - (2) = +	7,000	13,800	16,400	26,300	11,000	23,800	15,900

TABLE II.

Reaction	Base						
	CdO	PbO	CuO	HgO	Tl <sub>2</sub> O	Cu <sub>2</sub> O	Ag <sub>2</sub> O
[Base, H <sup>+</sup> S] (1)	32,100	34,000	36,500	50,000	43,300	43,300	63,300
[Base, 2HCl] (2)	55,000	50,000	50,000	53,500	62,200	49,300	77,200
(1) - (2) = -	22,900	16,000	13,500	3,500	18,900	6,000	13,900

TABLE III.

Reaction	Base					
	MnO.H <sub>2</sub> O	FeO.H <sub>2</sub> O	NiO.H <sub>2</sub> O	CoO.H <sub>2</sub> O	ZnO.H <sub>2</sub> O	
[Base 2HClAq, H <sup>+</sup> SAq] } (1)	10,700	14,600	18,600	17,400	18,600	
[Base Aq, 2HClAq] } (2)	23,000	21,400	22,600	21,100	20,300	
(1) - (2) = -	12,300	6,800	4,000	3,700	1,700	

<sup>1</sup> See Naumann, *Thermochemie*, 495 and 501.

<sup>2</sup> See Naumann, *loc. cit.* 505—510.

To illustrate the application of these data, take the case of cadmium.

$$[\text{CdO}_2\text{HClAq}, \text{H}^2\text{SAq}] = 27,300 :$$

i.e. the thermal value of the change which occurs when aqueous  $\text{H}_2\text{S}$  reacts on a dilute solution of  $\text{CdO}$  in  $\text{HCl}$  is represented by 27,300 units +.

$$[\text{CdOAq}, 2\text{HClAq}] = 20,300 :$$

i.e. the thermal value of the change which occurs when  $\text{CdO}$  in aqueous solution is neutralised by a dilute solution of  $\text{HCl}$  is represented by 20,300 units +. The former number exceeds the latter by 7,000,  $\therefore$  the action of  $\text{H}_2\text{S}$ , in solution, on  $\text{CdO}$ , in dilute  $\text{HCl}$  solution, is accompanied by evolution of 7,000 units of heat; this action readily occurs. But

$$[\text{CdO}, \text{H}^2\text{S}] = 32,100 ; \text{ and } [\text{CdO}, 2\text{HCl}] = 55,000 :$$

i.e. the formation of  $\text{CdS}$ , by the action of gaseous  $\text{H}_2\text{S}$  on  $\text{CdO}$ , is accompanied by the evolution of 22,900 units of heat less than attends the action of gaseous  $\text{HCl}$  on  $\text{CdO}$ ,  $\therefore$   $\text{CdS}$  is decomposed by gaseous  $\text{HCl}$  with formation of  $\text{CdCl}_2$ .

Moreover the numbers

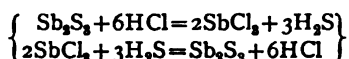
$$[2\text{HCl}, \text{Aq}] = 34,600 ; \text{ whereas } [\text{H}^2\text{S}, \text{Aq}] = 4,800$$

shew, that, comparing equivalent quantities of hydrochloric acid and sulphuretted hydrogen, the former when in the state of gas possesses an excess of energy, measured by about 34,000 thermal units, above what it possesses when in dilute solution, whereas the excess of energy of gaseous  $\text{H}_2\text{S}$  above that possessed by  $\text{H}_2\text{S} \cdot x\text{H}_2\text{O}$  is measured by about 5000 thermal units. But the more concentrated an aqueous solution of hydrochloric acid, the less is the quantity of heat evolved by adding hydrochloric acid gas to that solution; in other words, a concentrated aqueous solution of this acid is nearly as energetic a reagent, provided it is used in sufficient quantity, as gaseous hydrochloric acid. Hence we should conclude, and our conclusion is verified by experiment, that cadmium sulphide will be decomposed by concentrated aqueous hydrochloric acid.



The case of antimony is especially interesting.

Antimony sulphide is decomposed by aqueous hydrochloric acid of greater concentration than  $\text{HCl} \cdot 6\text{H}_2\text{O}$ ; but if more water than this is present, antimony chloride is decomposed by sulphuretted hydrogen. Hence the two reactions



may occur until a state of equilibrium is established, which is conditioned by the relative energies of the components, and this again is conditioned by the relative masses of these components, temperature being constant throughout.

A consideration of Table III. shews, that the heat of neutralisation by  $2\text{HCl}$  of any of the bases in that table is greater than the heat evolved during the action of  $\text{H}_2\text{S}$  on such neutralised solutions; we should not therefore expect sulphuretted hydrogen to precipitate the metals in this table from dilute acid solutions. But if ammonia (or soda) is added to such solutions, the hydrochloric acid is neutralised rather than the sulphuretted hydrogen, because

$$[(\text{NH}_4)^2\text{Oaq}, \text{H}^2\text{SAq}] = 6,300 : \text{ but } [(\text{NH}_4)^2\text{Oaq}, 2\text{HClAq}] = 24,700.$$

Under these conditions the base is precipitated as sulphide<sup>1</sup>.

The energetic action of antimony pentachloride as a chlorinating agent is in keeping with the thermal values obtained by Thomsen<sup>2</sup>, viz.

$$[\text{Sb}, \text{Cl}^2] = 91,400 ; \text{ but } [\text{SbCl}_5, \text{Cl}^2] = 13,500,$$

These numbers shew that the formation of the molecule  $\text{SbCl}_5$ , from  $\text{SbCl}_3$  and  $\text{Cl}_2$ , is attended with a loss of energy much less than two-thirds of that lost in the formation of the molecule  $\text{SbCl}_3$  from  $\text{Sb}$  and  $\text{Cl}_2$ .

122. We have been accustomed to regard most processes of chemical change as consisting of two parts, (1) decomposition of the molecules forming the initial system, (2) rearrangement of the atoms thus produced to form the new molecules which compose the final system. The first part of a change,

<sup>1</sup> For more details see Naumann, *loc. cit.*

<sup>2</sup> See *Thermochemische Untersuchungen*, 2. 332—4.

as thus regarded, must be accompanied by gain of energy to the entire system, and the latter part by loss of energy. The gain may exceed the loss, or *vice versa*; the process as a whole may be endothermic or exothermic. In the preceding paragraphs of this section no attempt has been made to separate the thermal values of these two parts of any change, the numbers given in these paragraphs represent the algebraic sums of two or more quantities. In some cases the chemical changes are represented in formulæ which are undoubtedly molecular, but in most cases we have dealt with solid or liquid substances, and the thermal values assigned to the various changes must therefore be generally regarded as only measuring the quantities of heat evolved or absorbed during the reactions, as defined in the equations, between those masses of the various chemical substances which are expressed by their formulæ when read in grams.

But if relative measurements of the gains of energy which accompany the formation of atomic, from molecular systems, could be obtained, much light would certainly be thrown on many questions which have been discussed or alluded to in preceding chapters.

123. Thomsen<sup>1</sup> has attempted to calculate the quantity of heat required to separate the molecule of carbon, assumed to be diatomic, into atoms; his results and methods will be discussed hereafter (par. 134). Meanwhile we may note that what Thomsen calls the 'heat of dissociation' of a carbon atom is supposed to be equal to about 37,000 gram-units.

E. Wiedemann<sup>2</sup> has measured the heat required to change the 'band spectrum' of hydrogen into the 'line spectrum'; and, on the assumption that the 'line spectrum' is associated with vibrations of atoms and the 'band spectrum' with vibrations of molecules, he has calculated that about 128,000 gram-units of heat are required in order to separate 1 gram-molecule of hydrogen into its constituent atoms; and that

<sup>1</sup> *Ber.* 13. 1321 and 1388. *Do.* 15. 328. See also *Thermochemische Untersuchungen*, 2. 101 *et seq.*

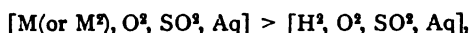
<sup>2</sup> *Wied. Ann.* [2] 5. 500, and *do.* 18. 509.

a greater quantity of heat than this is required in the case of the molecule of nitrogen.

Thomsen and Wiedemann have shewn that more energy is almost certainly associated with a mass of hydrogen, nitrogen, or gaseous carbon, when the greater part of the matter is in the state of atoms than when in the state of molecules; in other words, their investigations furnish physical evidence in favour of the generally adopted explanation of nascent actions.

124. The actions of metals on acids were considered in Chap. II. pars. 42 to 44. Thermal measurements help to elucidate these actions.

If the heats of formation in aqueous solution of the sulphates of silver, thallium, copper, cadmium, mercury, nickel, cobalt, iron, manganese, and zinc, are compared with the heat of formation of sulphuric acid in aqueous solution, it is found that the former values are greater than the latter except in the cases of copper and silver: i.e. for the heavy metals



except when  $M = Cu$  or  $M_2 = Ag_2$ ; hence we should expect the heavy metals, except copper and silver, to decompose dilute sulphuric acid with evolution of hydrogen.

When  $M_2 = Tl_2$ , the positive value of the difference in question is not large (1,900 units), hence the action between this metal and dilute sulphuric acid does not proceed rapidly. But when the acid is concentrated action is more energetic, inasmuch as the heat of solution of  $H_2SO_4$  is large;



But as a given mass of concentrated sulphuric acid contains considerably more energy than the same mass of dilute acid, it follows that the concentrated acid will probably be less chemically stable than the dilute.

The action of thallium on the concentrated acid results in the production of some sulphur dioxide. Now the change  $H_2SO_4 + H_2 = SO_2 + 2H_2O$  (assuming that this expresses the origin of the sulphur dioxide) is accompanied by the evolu-

tion of 14,900 units of heat. This change is represented thermally thus,

$$\begin{aligned} [\text{H}^2\text{SO}^4, \text{H}^2] &= [\text{S}, \text{O}^2] + 2[\text{H}^2, \text{O}] - [\text{S}, \text{O}^2, \text{O}^2, \text{H}^2] \\ &= 2[\text{H}^2, \text{O}] - [\text{SO}^2, \text{O}^2, \text{H}^2]. \end{aligned}$$

If the temperature is raised the acid becomes more concentrated, and at a certain stage sulphuretted hydrogen is evolved. This action is thermally probable, because

$$\begin{aligned} [\frac{1}{2}\text{H}^2\text{SO}^4, \text{H}^2] &= [\text{H}^2, \text{O}] + \frac{1}{2}[\text{H}^2, \text{S}] - \frac{1}{2}[\text{H}^2, \text{S}, \text{O}^4] \\ &= [\text{H}^2, \text{O}] - \frac{1}{2}[\text{H}^2\text{S}, \text{O}^4] \\ &= 23,700 \text{ units} +. \end{aligned}$$

A similar treatment of the action of copper on sulphuric acid shews that this metal would probably not decompose the acid when dilute, but that the metal might be expected to react slowly on concentrated acid, provided one of the products were sulphur dioxide; because



when expanded thermally, is

$$\begin{aligned} [\text{Cu}, \text{SO}^2, \text{O}^2] + 2[\text{H}^2, \text{O}] - 2[\text{H}^2, \text{O}^2, \text{SO}^2] \\ = 4,500 \text{ units} +. \end{aligned}$$

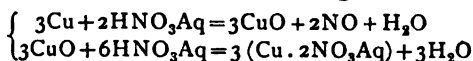
The quantity of heat set free in this action will in reality considerably exceed 5000 units, because heat will be evolved by the action between the  $\text{H}_2\text{SO}_4$  and  $2\text{H}_2\text{O}$  produced in the change; the amount of heat thus liberated may amount to as much as 8,000 or 9,000 units per gram-molecule of water.

The fact that  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  combine to form a series of hydrates, the production of each of which is marked by the evolution of heat, complicates such calculations as those given above. The relations between the masses of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  employed will certainly condition the direction and progress of the change. Starting with the system  $\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O} + x\text{H}_2$ , for a certain concentration of acid the final configuration will be  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , for another concentration of acid it will rather be  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$ , or  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2\text{O}$ . The action will also of course be conditioned by temperature.

If the foregoing considerations are correct, it follows that any metal which decomposes dilute sulphuric acid with evolution of hydrogen, ought, under certain conditions of temperature and concentration of acid, to decompose this acid with production of sulphuretted hydrogen or sulphur dioxide: zinc and tin certainly do produce both of these gases by their action on hot concentrated sulphuric acid.

A comparison of the heats of formation of nitrates of the heavy metals with the heat of formation of nitric acid, leads to the expectation that these metals, with the exception of silver, lead, thallium, copper and mercury, would decompose dilute nitric acid with production of hydrogen; but as the excess of heat evolved in this decomposition over that absorbed in separating  $\text{HNO}_3\text{Aq}$  into  $\text{NH}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ , &c. is large, we should expect the gaseous products of the reaction to consist for the most part of these compounds. The statement may be put thus; the initial system is metal and dilute nitric acid; the final possible system is metallic nitrate, oxides of nitrogen (or ammonia), and water; an intermediate stage is metallic nitrate and hydrogen; in the passage to the final system much more energy is lost than if the change stopped at the intermediate stage, therefore the change proceeds to what may be called its natural close.

If copper, mercury, or silver could act on dilute nitric acid so as to withdraw a portion of the oxygen of the acid, such action would be accompanied by a considerable loss of energy, and would therefore be thermally probable. The formation of nitric oxide would absorb more heat than that of any other possible product of this change; but the necessary amount of heat is evolved in the action of copper, or mercury, on dilute nitric acid; therefore the change



is thermally possible, assuming the first part to consist of a deoxidising action of copper on the acid. The occurrence of a similar change when copper or mercury is replaced by silver becomes thermally probable only when the acid is tolerably concentrated.

Thermal measurements appear then to indicate differences between the action of zinc, magnesium, nickel, &c., and that of copper, mercury, and silver, on dilute nitric acid. The gaseous products of the action of the first class of metals are probably for the most part the results of secondary changes occurring between nascent hydrogen and the acid, whereas the same substances when arising from the action of metals of the second class may rather be regarded as the results of a direct deoxidising action exerted by the metal on the acid<sup>1</sup>.

Traube, as we found in chapter II. (pars. 43, 44), from investigations conducted on lines very different from those of thermal chemistry, was led to regard the action of copper on nitric acid as essentially a deoxidising action.

125. From what we have learned regarding atomic and molecular systems, and from a consideration of the preceding paragraphs of this section, it follows almost necessarily that change from one allotropic modification of an element to another must be accompanied by absorption or evolution of heat. A few thermal measurements are given here to shew that this conclusion is fully justified by facts.

A.  $[P^2, O^6] = 369,100 \text{ units} +$  when  $P_2$  is 62 grams of ordinary phosphorus ( $P^a$ );

$[P^2, O^6] = 326,800 \text{ units} +$  when  $P_2$  is 62 grams of amorphous phosphorus ( $P^b$ );

$\therefore$  the change of  $P^a$  to  $P^b = 21,150 \text{ units of heat} +$ .

In the oxidation of 31 grams  $P^a$  to  $H_3PO_4$  in aqueous solution by hypochlorous acid, 209,500 thermal units are evolved;

in the oxidation of 31 grams  $P^b$  to  $H_3PO_4$  in aqueous solution by hypochlorous acid, 181,200 thermal units are evolved;

$\therefore$  the change of  $P^a$  to  $P^b = 28,300 \text{ units of heat} +$ .

Hence mean value of this change = 24,725 gram-units +.

B.  $[2O_2 = 3O_2] = 59,200 \text{ units of heat} +$ ; that is to say

the separation of 2 gram-molecules of ozone ( $O_3$ ) into 3 gram-molecules of oxygen ( $O_2$ ) is attended by the evolution of 59,200 units of heat.

<sup>1</sup> For thermal details concerning the action of metals on sulphuric and nitric acids see Naumann, *loc. cit.* 477-482.

The comparative thermal instability of the molecule  $O_3$  helps us to understand why ozone is so much more active as an oxidising agent than ordinary oxygen<sup>1</sup>.

C. If  $S_\alpha$  represent 32 grams of octahedral sulphur,  $S_\beta$  the same mass of prismatic,  $S_\gamma$  the same mass of soluble amorphous, and  $S_\delta$  the same mass of insoluble amorphous sulphur; then

				80 units of heat ;
	$S_\gamma$ to $S_\alpha$	„	„	absorption of
				80 units of heat ;
and	$S_\beta$ to $S_\alpha$	„	„	evolution of
				80 units of heat <sup>2</sup> .

126. Too little has as yet been done to allow of the application of thermal measurements to the classification of the elements in any but a very general way.

The relations existing between the members of a group of elements are sometimes summarised in the thermal values of comparable reactions undergone by these elements. Thus, (see table p. 240) taking Mendelejeff's group II. we have,

Series							
4	6	8	3	5	7	9	11
Ca	Sr	Ba	Mg	Zn	Cd	—	Hg
atomic weights	40	87	137	24	65	112	200.

The heats of formation in aqueous solution of the haloid salts of these metals are arranged in the following table (data from Naumann's book) :

	[M, Cl <sup>2</sup> , Aq]	[M, Br <sup>2</sup> , Aq]	[M, I <sup>2</sup> , Aq]
Ca	187,600	165,800	135,300
Sr	195,700	173,800	143,400
Ba	196,300	174,400	144,000
—	—	—	—
Mg	186,900	165,000	134,600
Zn	112,800	90,900	60,500
Cd	96,300	74,400	44,000
—	—	—	—
Hg	59,900	?	?

<sup>1</sup> According to van der Meulen (*Ber.* 18. 1853) the thermal value of the change in question,  $2O_3 = 3O_2$ , is about 68,000 units.

<sup>2</sup> For more details see Naumann, *loc. cit.* 486.

Hence we conclude that in each case the value for  $Ba > Sr > Ca > Mg$ , and for  $Mg > Zn > Cd > Hg$ . In other words, the thermal value of the change  $[M, X^2, Aq]$  increases as the atomic weight of  $M$  increases, when  $M$  is a member of an even series belonging to group II. but decreases as the atomic weight of  $M$  increases, when  $M$  is a member of an odd series of the same group. The difference between the values of  $[M, X^2, Aq]$  for each pair of elements is nearly constant. Thus

	$X=Cl$	$X=Br$	$X=I$
Ba - Sr =	600	600	600
Sr - Ca =	8,100	8,000	8,100
Ca - Mg =	700	800	700
—	—	—	—
Mg - Zn =	74,100	74,100	74,100
Zn - Cd =	16,500	16,500	16,500
Cd - Hg =	36,400	?	?

The close relationship of magnesium to calcium, and also its relations to barium and strontium, and the comparatively feebly marked relations existing between magnesium, zinc, cadmium, and mercury, are brought into forcible relief by these numbers<sup>1</sup>.

127. The comparative study of classes of compounds, no less than that of classes of elements, has already been considerably advanced by the application of thermal methods. Thus the relations between the oxides and oxyacids of nitrogen, phosphorus, and arsenic are suggested by the following data

$[N^2, O^3, Aq] = 6,800 \text{ units} - .$	$[P^2, O^3, Aq] = 250,000 + .$
$[N^2, O^6, Aq] = 29,800 \text{ ,, } + .$	$[P^2, O^6, Aq] = 405,500 + .$
$[N^2O^3Aq, O^2] = 36,600 \text{ ,, } + .$	$[P^2O^3Aq, O^2] = 155,500 + .$
$[As^2, O^3, Aq] = 147,100 + .$	
$[As^2, O^6, Aq] = 225,400 + .$	
$[As^2O^3Aq, O^2] = 78,300 + .$	

<sup>1</sup> Attention has already been drawn to the fact that there exists a well-marked connection of a periodic character between the atomic weights of the elements and their heats of combination with chlorine, bromine, and iodine. (See *ante*, par. 109.)



The superior thermal stability of the oxides of arsenic as compared with the analogous compounds of nitrogen, and the comparatively very great stability of the oxides of phosphorus, are rendered evident by these numbers. A comparison of the heats of formation of nitric, phosphoric and arsenic acids (although the formula of the first is not strictly comparable with that of the second and third), establishes the same point. Thus

$$[N, O^3, H, Aq] = 49,100 + : \quad [P, O^4, H^3, Aq] = 305,300 + : \\ [As, O^4, H^3, Aq] = 215,200.$$

If the heats of formation of the three oxyacids of phosphorus are compared, it is seen that the change from hypophosphorous, or phosphorous, to phosphoric acid, is thermally very probable,

$$[P, O^4, H^3, Aq] = 305,300 : \quad [P, O^3, H^3, Aq] = 227,600 : \\ [P, O^2, H^3, Aq] = 139,800.$$

A comparison of the thermal changes accompanying the formation and decomposition of the trichlorides of phosphorus, arsenic, antimony, and bismuth serves to illustrate the relations which exist between analogous chemical changes, and gains or losses of energy by the changing systems.

$$[P, Cl^3] = 75,300 : [As, Cl^3] = 71,500 : [Sb, Cl^3] = 91,400 : [Bi, Cl^3] = 90,600. \\ [PCl^3, Aq] = 65,100 ; \text{ giving } H_3PO_3 + 3HCl. \\ [AsCl^3, Aq] = 17,600 ; \quad " \quad \frac{As_2O_3 \cdot 3H_2O + 6HCl}{2}. \\ [SbCl^3, Aq] = 7,700 ; \quad " \quad \frac{Sb_2O_3 \cdot 3H_2O + 6HCl}{2}. \\ [BiCl^3, Aq] = 7,800 ; \quad " \quad BiOCl \cdot H_2O + 2HCl.$$

In the decomposition of  $SbCl_3$  by water, the greatest development of heat (8,900 units) corresponds to the formation of the oxychloride  $Sb_2O_3Cl_3$ ; the further change of this substance to  $Sb_2O_3$  and  $HCl$  involves absorption of a little heat.

$$\text{Now } [BiOCl, Aq] = -14,200, \text{ if } \frac{Bi_2O_3 + 2HCl}{2} \text{ is produced :}$$

$$\therefore [BiCl_3, Aq] = 7,800 - (-14,200) \left. \vphantom{\begin{matrix} \\ \end{matrix}} \right\} \text{ if } \frac{Bi_2O_3 \cdot 3H_2O + 6HCl}{2}$$

were produced.

These numbers associate the stability of  $\text{BiOCl}$  with great loss of energy in the formation of this compound.

Another way of stating the thermal reactions of analogous antimony and bismuth hydroxides illustrates the fact, that while antimony hydroxides are acid substances the corresponding bismuth compounds are marked by basic characters.

Thus  $[2\text{SbO}^3\text{H}^3, \text{HClAq}] = 2,400$ ; (forming  $\text{Sb}_4\text{O}_5\text{Cl}_2$ ):

but  $[\text{BiO}^3\text{H}^3, \text{HClAq}] = 14,200$ ; (forming  $\text{BiOCl}$ ).

The complete decomposition of a haloid salt by water may produce either hydroxide, hydrochloric acid, and water; or oxide, hydrochloric acid, and water. Taking the latter case, Thomsen has calculated the difference between the heats of formation, in presence of water, of oxides and chlorides, and has shewn that for all the nonmetals, except tellurium, antimony (trichloride), and bismuth, this difference is positive. We are not concerned here with tellurium; for antimony and bismuth the differences are

$$\frac{1}{2}[\text{Sb}^3, \text{O}^3, \text{H}^3\text{O}] - [\text{Sb}, \text{Cl}^3] = 7,680 \text{ units} - .$$

$$\cdot \frac{1}{2}[\text{Bi}^3, \text{O}^3, \text{H}^3\text{O}] - [\text{Bi}, \text{Cl}^3] = 21,700 \text{ ,, } - .$$

Hence we should conclude that  $\text{SbCl}_3$  and  $\text{BiCl}_3$  would differ from other analogous chlorides in being only partially decomposed by water, and that the decomposition would be carried further in the case of antimony than in that of bismuth. This expectation is confirmed by the actually occurring reactions<sup>1</sup>; in the case of  $\text{SbCl}_3$ ,  $\frac{5}{8}$ ths of the total decomposition (i. e. decomposition into oxide, hydrochloric acid, and water) is accomplished by the formation of  $\text{Sb}_4\text{O}_5\text{Cl}_2$ ; in the case of  $\text{BiCl}_3$ , the formation of  $\text{BiOCl} \cdot \text{H}_2\text{O}$  represents  $\frac{2}{3}$ rds of the total decomposition.

A comparative study of some of the thermal relations of the hydracids and oxyacids of the halogens helps towards a classification of the latter group of acids<sup>2</sup>.

<sup>1</sup> For more details see Thomsen, *Thermochemische Untersuchungen*, 2. 25—39; 298—304; and 364—374.

<sup>2</sup> See Thomsen, *loc. cit.* 1. 150—155, and 240—253; also Jahn, *loc. cit.* 136—138.

The close thermal analogy between the hydracids in question is exhibited by these, among other, numbers ;

[HX, Aq]	[HXAq, NaOHAq]
$X = \text{Cl} = 17,400$	$X = \text{Cl} = 13,700$
$X = \text{Br} = 19,900$	$X = \text{Br} = 13,700$
$X = \text{I} = 19,200.$	$X = \text{I} = 13,700.$

But when we compare the heats of formation of these acids, in aqueous solutions, we find that the value of this constant for each acid decreases as the atomic weight of the halogen increases : thus

[H, X, Aq]
$X = \text{Cl} = 39,300$
$X = \text{Br} = 28,400$
$X = \text{I} = 13,200.$

The three oxyacids corresponding, in composition, to the three hydracids, are  $\text{HClO}_3$ ,  $\text{HBrO}_3$ , and  $\text{HIO}_3$ . The following numbers shew that, in some respects at any rate, the thermal relations between  $\text{HClO}_3$  and  $\text{HBrO}_3$ , are analogous to those between  $\text{HCl}$  and  $\text{HBr}$  :—

[H, X, O <sup>3</sup> , Aq]
$X = \text{Cl} = 23,900$
$X = \text{Br} = 12,400 :$

hence the difference,  $[\text{H, Cl, Aq}] - [\text{H, Br, Aq}]$ , is approximately equal to the difference  $[\text{H, Cl, O}^3, \text{Aq}] - [\text{H, Br, O}^3, \text{Aq}]$ .

From this we might provisionally conclude that the difference between the heats of formation, in aqueous solutions, of chloric and iodic acids, would probably be nearly the same as the difference between the heats of formation, under the same conditions, of hydrochloric and hydriodic acids. The value of the second difference is 26,100; hence, on this supposition, the first difference should be about 26,000. Now,

$$[\text{H, Cl, O}^3, \text{Aq}] = 23,900 ;$$

$$\therefore [\text{H, I, O}^3, \text{Aq}] = - 2,100.$$

But experiment shews that

$$[\text{H, I, O}^3, \text{Aq}] = + 55,700.$$

Hence it is evident that iodic acid differs in the most marked manner from bromic and chloric acids. This difference

is accentuated in the numbers expressing the heats of formation of these three acids from the three hydracids: thus,



$$X = \text{Cl} = 15,400 - .$$

$$X = \text{Br} = 15,900 - .$$

$$X = \text{I} = 42,600 + .$$

Iodic acid is probably dibasic, and may be represented by the formula  $\text{H}_2\text{I}_2\text{O}_6$ <sup>1</sup>.

128. A comparison of the mutual thermal actions of acids and bases throws considerable light on the classification of the substances which are included under these terms. The first volume of Thomsen's *Untersuchungen* is devoted to a consideration of this subject.

'Heat of neutralisation of an acid by a base' is defined as, the quantity of heat evolved on mixing equivalent quantities, in grams, of the acid and base, in dilute aqueous solutions, the products of the action being also soluble in water.

Thomsen employs a solution of  $2\text{NaOH}$  in about  $200 \text{ H}_2\text{O}$  (grams), and adds the acid solution diluted to a similar degree, temperature being  $18^\circ$ — $19^\circ$ ; in other words he determines the thermal value of the change

$[2\text{NaOHAq}, 2\text{HXAq}]$  in the case of a monobasic acid,

$[2\text{NaOHAq}, \text{H}_2\text{XAq}]$  „ dibasic „

$[2\text{NaOHAq}, \frac{2}{3}\text{H}_3\text{XAq}]$  „ tribasic „

$[2\text{NaOHAq}, \frac{1}{2}\text{H}_4\text{XAq}]$  „ tetrabasic „

( $X$ =acid radicle)

Most of the general conclusions drawn by Thomsen, and others, belong more to chemical kinetics than to statics, but some of the generalisations may fitly be introduced here<sup>2</sup>.

The commoner acids may be broadly divided into four groups according to the values of their heats of neutralisation, as thus defined.

I. Those acids which have a heat of neutralisation approximately equal to 20,000 gram-units:—



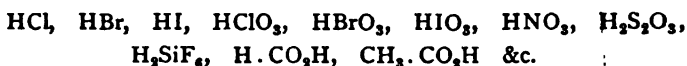
<sup>1</sup> See Thomsen, *Ber.* 7. 112 (or *Untersuchungen*, 2. 423).

<sup>2</sup> See especially for more details Thomsen, *loc. cit.* 1. 293—309, and 422—449.

II. Those acids which have a heat of neutralisation approximately equal to 25,000 gram-units:—

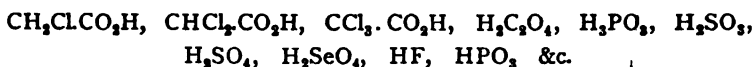


III. Acids the heat of neutralisation of which is equal to about 27,000 gram-units:—



Most of the acids belong to this class.

IV. Acids having a heat of neutralisation greater than 27,000 units, and varying from 28,000 to 32,500 units:—



A few acids have heat of neutralisation less than 20,000 units.

The value of the heat of neutralisation of an acid does not appear to depend on the basicity, nor on the composition of the acid; neither does it depend on what Thomsen calls the '*avidity*' of the acid, i.e. the striving of the acid to displace another from combination with a base. The relative '*avidities*' of acids will be considered in book II<sup>1</sup>, meanwhile the meaning of the term may be made clear by an example. When equivalent quantities of NaOH, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> are mixed in dilute aqueous solutions, two-thirds of the NaOH are found to combine with the HNO<sub>3</sub>, and one-third with the H<sub>2</sub>SO<sub>4</sub>. Hence HNO<sub>3</sub> is said to have an '*avidity*' for NaOH twice as great as that of H<sub>2</sub>SO<sub>4</sub> for the same base; HNO<sub>3</sub> in aqueous solution is therefore a '*stronger*' acid than H<sub>2</sub>SO<sub>4</sub>.

The basicity of an acid may be determined by thermal methods. One gram-molecule of the acid in dilute aqueous solution is mixed with  $\frac{1}{2}$ ,  $\frac{1}{3}$ ,  $\frac{1}{4}$ , 1, 2, &c. gram-molecules of NaOH also in dilute solution, and the heat evolved in the reactions is measured. (The ordinary formulæ NaOH, H<sub>2</sub>SO<sub>4</sub>, &c. are here assumed, for the sake of convenience of nomenclature, to be molecular). Comparing in this way HCl, H<sub>2</sub>SO<sub>4</sub>, and C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> (citric acid), we have this result,

<sup>1</sup> Chap. III. par. 233.

$[\text{HClAq}, \frac{1}{2}\text{NaOHAq}]$	= about 6,000	$[\text{H}^2\text{SO}^4\text{Aq}, \frac{1}{2}\text{NaOHAq}]$	= about 7,000
$[\text{HClAq}, \text{NaOHAq}]$	= 13,500	$[\text{H}^2\text{SO}^4\text{Aq}, \text{NaOHAq}]$	= 14,500
$[\text{HClAq}, 2\text{NaOHAq}]$	= 13,500	$[\text{H}^2\text{SO}^4\text{Aq}, 2\text{NaOHAq}]$	= 31,000
		$[\text{H}^2\text{SO}^4\text{Aq}, 3\text{NaOHAq}]$	= 31,000
$[\text{C}_6\text{H}_8\text{O}_7\text{Aq}, \text{NaOHAq}]$	= 12,400		
$[\text{C}_6\text{H}_8\text{O}_7\text{Aq}, 2\text{NaOHAq}]$	= 24,800		
$[\text{C}_6\text{H}_8\text{O}_7\text{Aq}, 3\text{NaOHAq}]$	= 38,000		
$[\text{C}_6\text{H}_8\text{O}_7\text{Aq}, 4\text{NaOHAq}]$	= 38,000.		

Hence we conclude that  $\text{HCl}$  is a monobasic,  $\text{H}_2\text{SO}_4$  a dibasic, and  $\text{C}_6\text{H}_8\text{O}_7$  a tribasic acid.

The application of this method to the oxyacids of phosphorus and arsenic leads to interesting results<sup>1</sup>.

The data are presented in the following table:—

$[\text{H}^3\text{PO}^3\text{Aq}, x\text{NaOHAq}]$		<i>Difference.</i>
$x = \frac{1}{2} = 7,400$		
$x = 1 = 15,000$	$x = 1 = 14,800$	7,400
$x = 2 = 15,000.$	$x = 2 = 28,500$	13,700
	$x = 3 = 28,900.$	400.
$[\text{HPO}^3\text{Aq}, x\text{NaOHAq}]$		
$x = 1 = 14,400.$		
$x = 2 = 14,800$ (about).		

The heat of neutralisation of this acid gradually increases till it becomes equal to about 33,600 units.

$[\text{H}^3\text{PO}^4\text{Aq}, x\text{NaOHAq}]$	<i>Difference.</i>	$[\text{H}^4\text{P}^2\text{O}^7\text{Aq}, x\text{NaOHAq}]$	<i>Difference.</i>
$x = \frac{1}{2} = 7,400$		$x = 1 = 14,400$	
$x = 1 = 14,800$	7,400	$x = 2 = 28,600$	14,200
$x = 2 = 27,100$	12,300	$x = 4 = 52,700$	24,100
$x = 3 = 34,000$	6,900	$x = 6 = 54,500.$	1,800.
$x = 6 = 35,300.$	1,300.		
$[\text{H}^3\text{AsO}^3\text{Aq}, x\text{NaOHAq}]$		$[\text{H}^3\text{AsO}^4\text{Aq}, x\text{NaOHAq}]$	
$x = 1 = 7,300$		$x = \frac{1}{2} = 7,400$	
$x = 2 = 13,800$	6,500	$x = 1 = 15,000$	7,600
$x = 4 = 15,000$	1,200	$x = 2 = 27,600$	12,600
$x = 6 = 15,600.$	600.	$x = 3 = 36,000$	8,400
		$x = 6 = 37,400.$	1,400.

<sup>1</sup> See Thomsen, *loc. cit.* 1. 201—205; and Jahn, *Die Grundsätze der Thermochemie*, 110—113.

Hypophosphorous ( $\text{H}_2\text{PO}_2$ ), and metaphosphoric ( $\text{HPO}_3$ ) acids are evidently monobasic; phosphorous ( $\text{H}_3\text{PO}_3$ ), and arsenious ( $\text{H}_3\text{AsO}_3$ ) acids are dibasic; orthophosphoric, and arsenic acids ( $\text{H}_3\text{PO}_4$  and  $\text{H}_3\text{AsO}_4$ ) are tribasic, and pyrophosphoric acid ( $\text{H}_4\text{P}_2\text{O}_7$ ) is tetrabasic. The gradual rise in the value of the heat of neutralisation of  $\text{HPO}_3$ , Aq is explained by the fact, that an aqueous solution of this acid is slowly decomposed with formation of  $\text{H}_3\text{PO}_4$ ; the final number obtained (33,600) therefore represents the neutralisation of  $\text{H}_3\text{PO}_4$ , and not of  $\text{HPO}_3$ . A comparison of the heats of neutralisation of  $\text{H}_3\text{PO}_3$  and  $\text{H}_3\text{AsO}_3$  shews that the former is a much 'stronger' acid than the latter. A similar comparison of  $\text{H}_3\text{PO}_4$  with  $\text{H}_3\text{AsO}_4$  however shews that these acids are very analogous. Thus, the heat of neutralisation of  $\text{H}_3\text{PO}_4 = 34,000$ , and of  $\text{H}_3\text{AsO}_4 = 36,000$ ; moreover about three-fourths of the total heat is evolved, in each case, during the replacement of the first and second atom of hydrogen by sodium; and finally the addition of an excess of soda over that required for neutralisation, causes the evolution of an appreciable quantity of heat. The last fact is explained by the comparative instability in aqueous solutions of  $\text{Na}_2\text{PO}_4$  and  $\text{Na}_2\text{AsO}_4$ , which salts are partially separated by water into  $\text{Na}_2\text{HPO}_4$  and  $\text{H}_3\text{PO}_4$ , and  $\text{Na}_2\text{HASO}_4$  and  $\text{H}_3\text{AsO}_4$ , respectively; hence the addition of more soda than is required to form either of these salts evolves a little heat, because it enters into reaction with the small quantity of phosphoric, or arsenic acid, present in the liquid. A similar phenomenon is noticed in the neutralisation of tetrabasic phosphoric acid; more than one-fourth of the total quantity of heat is evolved during the action of the first molecule of  $\text{NaOH}$ , and more than a half during the action of the first and second molecules. We should thence expect the tetrasodic salt to be less stable than the disodic salt; that this is so is shewn by the evolution of 1800 units of heat on addition of two molecules of soda more than the amount required for complete neutralisation<sup>1</sup>.

The polybasic acids may also be classified in accordance

<sup>1</sup> In these, and other similar reactions, for convenience of nomenclature, the formulæ  $\text{NaOH}$ ,  $\text{H}_2\text{SO}_4$ , &c. are regarded as molecular.

with the thermal value of the action of each gram-molecule of soda on one gram-molecule of acid. Thus, comparing oxalic with sulphurous acid, we find the difference between the quantities of heat evolved during the action of the first and second molecules of soda, in the case of oxalic acid to be 600, and in that of sulphurous acid to be 2750: the data are,

$$\begin{array}{l} \text{[H}^2\text{C}^2\text{O}^4\text{Aq, NaOHAq]} = 13,840 \\ \text{[H}^2\text{C}^2\text{O}^4\text{Aq, 2NaOHAq]} = 14,440 \end{array} \begin{array}{c} \text{Difference.} \\ \left. \begin{array}{l} \text{---} 600 ; 2750 \end{array} \right\} \end{array} \begin{array}{l} \text{[H}^2\text{SO}^3\text{Aq, NaOHAq]} = 15,850 \\ \text{[H}^2\text{SO}^3\text{Aq, 2NaOHAq]} = 13,100. \end{array}$$

Thomsen<sup>1</sup> divides the dibasic acids which he has examined into three groups:—

I. Those in the neutralisation of which each molecule of soda has the same thermal value: this group is at present represented by  $\text{H}_2\text{SiF}_6$ , and  $\text{H}_2\text{PtCl}_6$ <sup>2</sup>.

II. Those in the neutralisation of which the first molecule of soda has a smaller thermal value than the second, the difference between the two values varying from 450 to 1900 units: this group contains the acids  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{SeO}_4$ ,  $\text{H}_2\text{C}_2\text{O}_4$  and  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ .

III. Those in the neutralisation of which the first molecule of soda has a larger thermal value than the second, the difference between the two values varying from 1850 to 2750 units: the acids in this group are  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SeO}_3$ ,  $\text{H}_2\text{CO}_3$  and  $\text{H}_2\text{B}_4\text{O}_7$ ;  $\text{H}_2\text{CrO}_4$ ,  $\text{H}_2\text{PHO}_3$ , and  $\text{C}_2\text{H}_4(\text{CO}_2\text{H})_2$  also probably belong to this group, although the differences between the thermal values of the first and second molecule of soda are smaller in the case of these acids than of those already mentioned (see below).

*Data on which the foregoing classification is based.*

		GROUP I.			
Heat evolved in action of NaOH				$\text{H}_2\text{SiF}_6$	$\text{H}_2\text{PtCl}_6$ <sup>2</sup>
1st molecule	...	...		13,300	13,600
2nd "	...	...		13,300	13,600.

<sup>1</sup> *loc. cit.* 1. 302—306.

<sup>2</sup> But it seems doubtful whether the numbers obtained by Thomsen really represent the neutralisation of this acid. See *Thermochemische Untersuchungen*, I. 229.



## GROUP II.

Heat evolved in action of NaOH.	$H_2SO_4$	$H_2SeO_4$	$H_2C_2O_4$	$H_2C_4H_4O_8$
1st molecule	14,750	14,750	13,850	12,450
2nd "	16,650	15,650	14,450	12,850.

## GROUP III.

	$H_2SO_3$	$H_2SeO_3$	$H_2CO_3$	$H_2B_2O_4$
1st "	15,850	14,750	11,000	11,100
2nd "	13,100	12,250	9,150	8,900.

	$H_2CrO_4$	$H_2PHO_3$	$C_2H_4(CO_2H)_2$
1st "	13,150	14,850	12,400
2nd "	11,550	13,600	11,750.

The reaction between an acid and its normal salt is accompanied by absorption of heat when the acid belongs to Group II, and by evolution of heat when it belongs to Group III<sup>1</sup>. The tribasic acids examined by Thomsen are divisible into two groups, corresponding to the second and third groups of the dibasic acids: thus,

## GROUP II.

Heat evolved in action of NaOH		$H_3C_6H_3O_6$ (Aconic acid)	$H_3C_6H_5O_7$ (Citric acid)
1st molecule	...	12,850	12,650
2nd "	...	12,950	12,800
3rd "	...	13,350	13,550.

## GROUP III.

		$H_3AsO_4$	$H_3PO_4$
1st "	...	15,000	14,850
2nd "	...	12,600	12,250
3rd "	...	8,350	6,950.

Thomsen suggests (l. pp. 304-5) that the foregoing classification of dibasic and tribasic acids may be summarised in these typical formulæ:—

<sup>1</sup> Hydrofluoric acid acts on potassium fluoride with absorption of 370 gram-units of heat; it would appear to belong to Thomsen's second group. (See Guntz *Compt. rend.* 97. 256.)

*Dibasic Acids.*

Acid of Group I.	Typical formula	$RH_2$	e.g. $SiF_6H_2$ ;
" II.	"	$R(OH)_2$	e.g. $SO_2(OH)_2$ ;
" III.	"	$R(OH)H$	e.g. $SO_2(OH).H$ .

*Tribasic Acids.*

Acid of Group II.	Typical formula	$R(OH)_3$	e.g. $C_4H_5O_4(OH)_3$ ;
" III.	"	$HR(OH)H$	e.g. $HPO_3(OH).H$ .

The 'heat of neutralisation of a base' is defined by Thomsen<sup>1</sup> as the thermal value of the change which occurs when equivalent quantities of base and acid react in dilute aqueous solution, the products of the action being also soluble in water. A dilute solution of one gram-molecule of sulphuric acid (i.e. the amount of acid, in grams, expressed by the formula  $H_2SO_4$ ) is employed; temperature being  $18^\circ$ — $19^\circ$ .

In other words, Thomsen measures the thermal values of the following reactions:—

$[H^2SO^4Aq, 2MOHAq \text{ or } 2NX^3Aq]$	in the case of a monacid base,
$[H^2SO^4Aq, M(OH)_2Aq \text{ or } N^2X^6Aq]$	" diacid "
$[H^2SO^4Aq, \frac{2}{3}M(OH)_3Aq \text{ or } \frac{2}{3}N^3X^9Aq]$	" triacid "
$[H^2SO^4Aq, \frac{1}{2}M(OH)_4Aq \text{ or } \frac{1}{2}N^4X^{12}Aq]$	" tetracid "
$(X=H, \text{ or a radicle } C_nH_{2n+1})$	

The bases which are soluble in water may be divided into two thermal groups:—

I. The group of the hydrates or hydroxides, represented by  $NaOH$  and  $KOH$ .

II. The group of the anhydrous bases, represented by  $NH_3$ .

The first group comprises  $LiOH$ ,  $NaOH$ ,  $KOH$ , and  $TlOH$ ;  $Ca(OH)_2$ ,  $Sr(OH)_2$ , and  $Ba(OH)_2$ ;  $N(CH_3)_4OH$ ,  $(C_2H_5)_4S.OH$ , and  $Pt(NH_3)_4(OH)_2$ ; the mean value of the change  $[H^2SO^4Aq, 2MOHAq \text{ (or } M(OH)_2Aq)]$  is equal to 31,350 units +, when  $M(OH)$  or  $M(OH)_2$  is one of the bases of this group.

The second group comprises  $NH_3$  and the amines of the form  $NH_2(C_nH_{2n+1})$  and  $NH(C_nH_{2n+1})_2$ ; the mean value of

<sup>1</sup> See especially *loc. cit.* 1. 422—449.

the change  $[H^2SO^4Aq, 2NX^2Aq]$  is equal to 28,200 +, when  $NX^2$  is one of the bases of this group.

Substitution of negative radicles for H in  $NH_3$  causes a considerable decrease in the heat of neutralisation of the base ; thus,

$$\begin{aligned} [2NH^2(C^2H^5)Aq, H^2SO^4Aq] &= 15,500, \\ \text{and } [2NH^2(C^2H^7)Aq, H^2SO^4Aq] &= 15,200 ; \\ \text{also } [2NH^2OHAq, H^2SO^4Aq] &= 21,600. \end{aligned}$$

When CO is substituted for H in  $2NH_3$ , the heat of neutralisation of the product,  $[(NH_2)_2CO]$  is almost nil.

Measurements of the quantities of heat evolved during the action of acids on those bases which are insoluble in water shew great irregularities. The true heats of neutralisation of these bases cannot be determined. But from the analogies between the hydrates of barium, strontium, and calcium, and those of magnesium, zinc, and manganese<sup>1</sup>, Thomsen concludes that the heats of neutralisation of the bases of the magnesian class are equal to those of the bases of the alkaline earth metals ; but as the heats of neutralisation of the latter and of the alkalis are equal, Thomsen argues that the mean value of the heat of neutralisation of  $M(OH)_2$ , when  $M = Mg, Mn, Ni, Co, Fe, Cd, Zn, \text{ or } Cu$ , is 31,350 units.

From what has been said regarding the classification of acids in accordance with their heats of neutralisation<sup>2</sup>, it will be apparent that if  $2HClAq$  is substituted for  $H_2SO_4Aq$  in the preceding reactions, the mean heats of neutralisation of the two groups of bases will be represented by numbers smaller than 31,350 and 28,200 respectively.

The identity of the numbers expressing the heats of neutralisation of bases of such different composition as  $KOH$  and  $Pt(NH_3)_4(OH)_2$  points to the possibility of connecting similar changes of energy with similarity of chemical type, maintained through series of more or less unlike individuals. The heats of neutralisation of the bases  $MX_2$  also point to the existence of a relation between change of energy and

<sup>1</sup> See Thomsen, *loc. cit.* 1. 435—440.

<sup>2</sup> See *ante*, p. 280.

composition; but the influence of the structure of the individual substance is shewn in the small values obtained for  $\text{NH}_2(\text{C}_6\text{H}_5)$  and  $\text{NH}_2(\text{C}_7\text{H}_7)$ , in which, although the chemical type is maintained, the typical thermal value is widely departed from.

The quantity of heat evolved in the reaction  $[\text{2MOHAq}, \text{HXAq}]$  when  $\text{M} = \text{K}, \text{Na}, \&c.$  is nearly constant, whether  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ; but the value of the reaction  $[\text{PbO.H}_2\text{O}, \text{HXAq}]$ , or  $[\text{Ti}_2\text{O.H}_2\text{O}, \text{HXAq}]$  &c. differs very considerably according as  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ . In the reaction with  $\text{PbO.H}_2\text{O}$ , the thermal value is greatest for  $\text{HIAq}$ , and least for  $\text{HClAq}$ . Now in the reactions just mentioned, haloid salts are produced which are only slightly soluble: if the heats of solution of these salts are added to the values of the apparent heats of neutralisation of the bases, it is found that the true heats of neutralisation of  $\text{PbO.H}_2\text{O}$ ,  $\text{Ti}_2\text{O.H}_2\text{O}$  &c. are represented by the same number, whether  $\text{HClAq}$ ,  $\text{HBrAq}$ , or  $\text{HIAq}$  is the acid employed. If it is granted that the true heats of neutralisation of these acids are the same for other bases which form insoluble haloid salts, it becomes possible to calculate the heats of solution of these salts. Thomsen has done this for  $\text{PbCl}_2$ ,  $\text{PbBr}_2$ ,  $\text{PbI}_2$ ,  $\text{AgCl}$  &c. and, carrying out the same method, he has even given a value for the heat of solution of barium sulphate.

Thomsen's investigation of the heats of neutralisation of acids and bases serves to shew the complexity of many of the reactions to which thermal values are assigned, and also the necessity of making all the conditions of the changes we wish to study as exactly comparable as possible. At the same time it illustrates one of the dangers which beset the employment of thermal methods in chemistry, the danger namely of theorising regarding chemical changes which do not occur, and of speculating about chemical compounds which have no existence.

129. The primary aim of thermal chemistry was stated in par. 117 to be the measurement of the differences between the quantities of energy possessed by chemical systems when in certain definite initial and final states; the basis of these

measurements being, the deduction from the general theory of energy, which states, that the total loss of energy during the passage of a chemical system from a definite initial to a definite final state is independent of the intermediate states.

The application of this generalisation was illustrated in par. 120. We are now however in a position more fully to discuss the relations existing between gain or loss of heat, and gain or loss of energy by a chemical system. It will be advantageous to confine our consideration at present to gaseous substances. When heat is imparted to a gaseous system of chemical substances, a portion may be employed in increasing the kinetic energy of motion of the molecules, i.e. in raising the temperature, of the system; another portion may be employed in doing work against external forces, e.g. in causing expansion of the system; and another portion may do work against molecular and atomic forces, and so produce a rearrangement of molecules, or atoms, i.e. may cause chemical changes to proceed within the system. The exact manner of the distribution of the energy imparted in the form of heat will vary in each special case. It is evident that the thermal value of the purely chemical part of a change—say of the system  $2\text{H}_2 + \text{O}_2$  to the system  $2\text{H}_2\text{O}$ —will vary according to variations in the physical conditions under which the change proceeds, and more especially according to variations of temperature.

The difference between the energy of the system  $2\text{H}_2 + \text{O}_2$  and that of the system  $2\text{H}_2\text{O}$  (both in grams) at ordinary temperatures, say at  $15^\circ$ , is measured by 136,800 thermal units; what will be the value of the difference between the same systems at  $200^\circ$ ?<sup>1</sup>

Let  $Q_{15}$  and  $Q_{200}$  represent the two differences: let  $U$  = the quantity of heat which must be imparted to the first system ( $2\text{H}_2 + \text{O}_2$ ) in order to raise its temperature from  $15^\circ$  to  $200^\circ$ ; let  $V$  = the quantity of heat which must be imparted to the second system ( $2\text{H}_2\text{O}$ ) to raise its temperature through the same interval; then

$$Q_{200} = Q_{15} + U - V.$$

<sup>1</sup> See Naumann, *loc. cit.* 212, 213.



the second liquid; further let  $\gamma$  = specific heat of the liquid obtained by mixing  $A$  and  $B$ ; then the *calorimetric equivalents* of the three liquids are (1)  $A.\alpha = q_a$ , (2)  $B.\beta = q_b$ , (3)  $(A + B).\gamma = q_c$ . For small variations of temperature the values of the specific heats, and therefore of the calorimetric equivalents, may be regarded as independent of temperature. Then putting  $R_T$  as the thermal value of the change represented by  $[A, B]$  at temperature  $T$ , and  $R_t$  as the value of the same change of temperature  $t$  we get<sup>1</sup>

$$R_T - R_t = (T - t)(q_a + q_b - q_c).$$

And from this, the variation in the value of  $R$  for each degree of temperature may be found, by the equation

$$\Phi = \frac{R_T - R_t}{T - t} = q_a + q_b - q_c$$

This formula is applied by Thomsen to the reactions between acids and bases at varying temperatures<sup>2</sup>.

To obtain a perfectly general formula it would however be necessary to study the relation between the specific heat and the temperature of each solution employed, and also of the solution produced by the chemical change: it would also be necessary to know the relation between the variation in the value of the calorimetric equivalent of each solution and the composition of that solution, i.e. the relative number of gram-molecules of salt and water contained therein<sup>3</sup>. Thomsen's general conclusion<sup>4</sup>—based on the examination of the influence of water of dilution on  $H_2SO_4Aq$ ,  $HClAq$ ,  $NaOHAq$ ,  $Na_2SO_4Aq$ ,  $NaClAq$ ,  $Na_2SO_4.2HClAq$ , and  $H_2SO_4.2NaClAq$ —is, that the calorimetric equivalent of a solution mixed with water is always less than the sum of the calorimetric equivalents of the original solution and the added water: i.e.

$$q_c < (q_a + q_b) \text{ and } \therefore \Phi = \frac{d.Q}{d.t} = q_a + q_b - q_c > 0.$$

<sup>1</sup> See for details shewing how these formulæ are obtained, Thomsen, *loc. cit.* 66—67.

<sup>2</sup> *loc. cit.* 1. 68—70.

<sup>3</sup> Tabulated data bearing on both of these points will be found in Naumann, *loc. cit.* pp. 289—310.

<sup>4</sup> *loc. cit.* 1. 80—88.

E. Wiedemann has recently investigated the connection between the calorimetric equivalents of certain solutions and the relative quantities of salt and water contained therein<sup>1</sup>.

The calorimetric equivalent of a solution of a salt with molecular-weight, or rather formula-weight,  $M$ , dissolved in  $n$  molecules of solvent having molecular weight  $m$ , is evidently<sup>2</sup>  $c(M + nm)$ , when  $c$  = specific heat of the solution. Wiedemann finds that in the cases of aqueous solutions of sodium chloride, sulphate, and nitrate, and ammonium sulphate, the calorimetric equivalent (or it may be called the molecular heat, using the term 'molecular' as already defined) of very concentrated solutions is greater than that of the water contained therein; as the solutions are diluted, a point is reached at which the calorimetric equivalents of the solution and of the water therein become equal; and lastly the calorimetric equivalent of still more dilute solutions is less than that of the water alone. In other words, if the calorimetric equivalent of the water in the solution is  $18n$ , then

for concentrated solutions	$c(M + nm) > 18n$	for aqueous solutions of NaCl, Na <sub>2</sub> SO <sub>4</sub> , NaNO <sub>3</sub> & (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> .
for solutions of mean concentration	$c(M + nm) = 18n$	
for dilute solutions	$c(M + nm) < 18n$	

Wiedemann's results seem to give a general confirmation to those of Thomsen<sup>3</sup>.

The relations between the calorimetric equivalents, and therefore the relations between the thermal changes and the temperature, of solutions of hydrated and dehydrated salts are more complicated than those already considered. Thus, solutions made by dissolving (1) one gram-molecule of MgSO<sub>4</sub> in 100 gram-molecules of H<sub>2</sub>O, and (2) one gram-molecule of MgSO<sub>4</sub>·7H<sub>2</sub>O in 93 gram-molecules of H<sub>2</sub>O, contain the same

<sup>1</sup> *Wied. Ann.* 18. 608.

<sup>2</sup> The 'molecular' heat of the solid in solution may be determined by the help of this formula, provided the specific heat of the solvent is known: see Wiedemann, *loc. cit.*

<sup>3</sup> A general treatment of the influence of temperature on the thermal values of changes occurring between liquids will be found in Jahn, *loc. cit.* Appendix 3, 210—216.



quantities of  $\text{MgSO}_4$  and  $\text{H}_2\text{O}$ . Now from observations of the specific heat of solution (1) it is found that

$$c(\text{MgSO}_4 + 100 \text{H}_2\text{O}) = 1761.$$

But, knowing the specific heat of magnesium sulphate, viz.  $c(\text{MgSO}_4) = 27$ , we should calculate that

$$c(\text{MgSO}_4 + 100 \text{H}_2\text{O}) = 27 + (100 \times 18) = 1827.$$

On the other hand, if the specific heat of the hydrate  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  is determined, and from this, that of the solution  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 93\text{H}_2\text{O}$  is calculated, we get this result,

$$c(\text{MgSO}_4 \cdot 7\text{H}_2\text{O}) = 100, \therefore c(\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + 93\text{H}_2\text{O}) = 100 + (93 \times 18) = 1774.$$

The observed calorimetric equivalent is, in each case, less than that calculated on the assumption that the equivalent of a solution is equal to the sum of the equivalents of the salt and of the water; but the difference between the observed and the calculated values is smaller when the solution is made from the hydrated, than when it is made from the dehydrated salt<sup>1</sup>. Thomsen<sup>2</sup> considers various cases of this kind, and draws the general conclusion, that the change in the thermal value of the solution of a hydrated salt in water, as temperature increases, is smaller, the greater the amount of water of hydration in the salt.

When compounds other than hydrated salts, being either solids, liquids, or gases, dissolve in water, the value of the thermal change also varies according to changes of temperature, but this variation is sometimes positive and sometimes negative with reference to the temperature-change.

130. Any chemical reaction occurs only within certain limits of temperature; by passing beyond these limits it is sometimes possible to reverse the process both chemically and thermally, without altering the nature or masses of the reacting substances; thus,

at ordinary temperatures  $2\text{H}_2\text{O} + 2\text{Cl}_2 = 4\text{HCl} + \text{O}_2$  .....(1)

but at about  $200^\circ$   $4\text{HCl} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{Cl}_2$  .....(2);

<sup>1</sup> Hence it follows that the specific heat of the water in a solid hydrated salt is less than the specific heat of the same water when the salt is in solution. (Thomsen, *loc. cit.* 1. 71.)

<sup>2</sup> *loc. cit.* I. 70—74.

if reaction (1) is expanded thermally it becomes

$$[2\text{H}^2\text{O Aq}, 2\text{Cl}^2\text{Aq}] = 4[\text{H}, \text{Cl}, \text{Aq}] - 2[\text{H}^2, \text{O}, \text{Aq}] = 20,400 \text{ units} + :$$

if reaction (2) is treated in the same way we have

$$[4\text{HCl}, \text{O}^2] = 2[\text{H}^2, \text{O}] - 4[\text{H}, \text{Cl}] = 28,500 \text{ units} + (\text{at } 200^\circ).$$

When we deal with reactions between solids, or systems containing solids or liquids, the numbers obtained by measuring the total losses or gains of heat may lead to erroneous conclusions regarding the nature of the chemical reactions: thus we have already found that the loss of energy in the formation of the system  $2\text{H}_2\text{O}$ , from  $2\text{H}_2 + \text{O}_2$ , is represented by about 20,000 thermal units less, when the entire system is maintained throughout the reaction in the gaseous state, than when the final system is allowed to pass into the liquid state. Again any comparisons or contrasts instituted between hydrochloric, hydrobromic, and hydriodic acids from a consideration of these numbers,

$$[\text{H}, \text{Cl}] = 22,000 + ; [\text{H}, \text{Br}] = 8,440 + ; [\text{H}, \text{I}] = 6,050 -$$

must be accepted with great reserve, because no indication is given in these equations of the fact that at ordinary temperatures chlorine is a gas, bromine a liquid, and iodine a solid; the reactions formulated appear to be strictly comparable, whereas they really present wide differences. Another case in point is presented by these numbers,

$$(1) [\text{C}, \text{O}] = 28,600 + ; \quad (2) [\text{C}, \text{O}^2] = 97,000 +.$$

In (1) we have the thermal value of a reaction wherein 16 grams of gaseous oxygen combine with 12 grams of solid carbon to produce 28 grams of a gaseous compound; in (2) we have the thermal value of a reaction wherein the same weight of solid carbon combines with  $16 \times 2$  parts by weight of gaseous oxygen to produce a gaseous compound. The conclusion seems inevitable that the union of the second 16 grams of oxygen with carbon is attended with the evolution of much more heat than the union of the first 16 grams of the same gas. But the equation  $[\text{CO}, \text{O}] = 68,400$ , which represents the union of a second quantity of 16 grams of oxygen with 12 grams of carbon already combined with 16 grams of oxygen in a gaseous compound, at once negatives

this conclusion, and rather favours that which would regard the number 136,800 (i.e.  $68,400 \times 2$ ) as representing the true heat of combination of carbon, i.e. as representing the thermal value of the reaction  $C + O_2 = CO_2$ , when  $C = 12$  grams of gaseous carbon. The following numbers shew that there is a close analogy between the thermal reactions of gaseous CO and gaseous  $H_2$ ;

$$\begin{aligned} [C, O_2] - 2[CO, O] &= 97,000 - (2 \times 68,400) \\ &= -39,800, \\ \text{and } [C, O_2] - 2[H_2, O] &= 97,000 - (2 \times 68,400) \\ &= -39,800; \\ \therefore [CO, O] &= [H_2, O]; \text{ but } [H_2, O] = 68,400, \\ \therefore [CO, O] &= 68,400. \end{aligned}$$

This conclusion is confirmed by experiment. Now, the decomposition of gaseous  $CO_2$  by hot C has the same thermal value as that of gaseous  $H_2O$  by hot C; thus

$$\text{and } \begin{cases} [CO_2, C] = 2[C, O] - [C, O_2] \\ [H_2O, C] = [C, O] - [H_2, O] \end{cases} = -39,800.$$

Hence, it is probable that the thermal value of the formation of gaseous  $CO_2$  from gaseous C and  $O_2$  is double that of the formation of gaseous  $H_2O$  from gaseous  $H_2$  and O. But the latter value is 68,400, therefore the former is probably 136,800<sup>1</sup>.

131. Another point to be noticed in analysing thermal measurements of chemical processes is, that the ordinary notation usually represents a chemical change as a much simpler phenomenon than it really is. Most chemical reactions are accomplished only by employing 'an excess,' sometimes a large excess, of one or more of the reacting substances: thus the equation



would more nearly express the distribution of the masses of the reacting bodies if it were written

$$x AgCl + x' HI = x'' AgI + x'' HCl + (x - x'') AgCl + (x' - x'') HI.$$

<sup>1</sup> See Mendelejeff, abstract of Russian paper in *Ber.* 15. 1555; or *C. S. Journal, Abstracts* for 1882, 916.

Potilitzin has investigated this subject of the relations between the thermal value of a change and the masses of the changing substances<sup>1</sup>. The heat of formation of a metallic chloride is as a rule greater than that of the corresponding bromide,

$$[\text{MBr}, \text{Cl}] = [\text{M}, \text{Cl}] - [\text{M}, \text{Br}] > 0 :$$

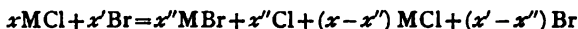
Again generally speaking it is true that

$$[\text{MBr}, \text{HCl}] = [\text{M}, \text{Cl}] + [\text{H}, \text{Br}] - [\text{M}, \text{Br}] - [\text{H}, \text{Cl}] < 0 ;$$

e. g.  $[\text{AgBr}, \text{HCl}] = 6,900 -$  ;  $[\text{KBr}, \text{HCl}] = 3,250 -$  ;  $[\text{NaBr}, \text{HCl}] = 1,600 -$ .

It would therefore appear probable that chlorine should decompose metallic bromides, but that hydrochloric acid should not react on these salts.

But Potilitzin's experiments shew that the reaction



proceeds at 275—300° when MCl and Br are employed in equivalent quantities, (M = K, Na, or Ag), and also that when MBr and Cl react in equivalent quantities the whole of the bromine is not replaced by the chlorine.

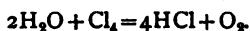
By increasing the amount of bromine, relatively to MCl, in the reaction above formulated, more MBr is produced until a limit is reached, whereat equilibrium is established. This equilibrium is not overthrown even by increasing the mass of bromine, raising the temperature, and prolonging the time of action.

132. I think the position has now been clearly established that the thermal value of a chemical change, even of a simple reaction between gaseous substances, really represents the sum of various changes, some of which have a positive and others a negative value. Assuming that in any case it is possible to separate the gain or loss of energy, measured thermally, during a definite chemical reaction, into a portion representing physical changes, and another portion representing purely chemical changes, it is nevertheless generally the case, that the latter portion of the total energy-change must itself be analysed, before an accurate and precise application of the thermal value can be made. For, assuming that

<sup>1</sup> See abstract in *Ber.* 14. 2044; and 15. 918; also 16. 3051.

we have made due allowance for the influence of the masses of the reacting substances, and for the possible formation and decomposition of molecular groups during the reaction, there yet remains the important consideration, that heat is absorbed or evolved, not only in decomposing, or producing, compounds, but also in reactions of decomposition or formation of elements, which take part in the chemical process.

Let us analyse a comparatively simple reaction ;



When this is expanded thermally we have

$$[2\text{H}^2\text{O}, 2\text{Cl}^2] = 4[\text{H}, \text{Cl}] + [\text{O}, \text{O}] - 2[\text{H}^2, \text{O}] - 2[\text{Cl}, \text{Cl}]$$

That is to say, heat is absorbed in separating each chlorine molecule into atoms, and heat is evolved in the union of each pair of oxygen atoms to form a molecule.

Let us take an apparently more simple instance

$$[\text{H}^2, \text{Cl}^2] = 44,000 \text{ units} +.$$

Remembering the fundamental distinction between atoms and molecules, and moreover bearing in mind the fact that the molecules of hydrogen and chlorine are both diatomic, we may expand this equation thus

$$[\text{H}^2, \text{Cl}^2] = 2[\text{H}, \text{Cl}] - [\text{H}, \text{H}] - [\text{Cl}, \text{Cl}] = 44,000.$$

But we do not know the true thermal value of any one of the three parts of this reaction ; when therefore we write  $[\text{H}^2, \text{Cl}^2] = 44,000$ , we express, in a shorter form, the fact, that when 2 grams of gaseous hydrogen combine with 71 grams of gaseous chlorine to produce 73 grams of gaseous hydrochloric acid, at ordinary temperatures, 44,000 gram-units of heat are evolved.

As long as thermal measurements are regarded in this way they convey precise and important information. But we want something more than this, we desire to have some light thrown on the rationale of chemical changes. Now our most far-reaching conceptions in chemistry are based on the distinction implied in the terms atom and molecule ; until then this distinction is practically recognised in thermal chemistry, we cannot expect any great advances to be made in applying the mass of data already accumulated to questions of chemical actions and reactions. The want of any means of determining

the thermal values of the decomposition of elementary molecules, and the combination of elementary atoms, is felt even more when an attempt is made to apply the data of thermal chemistry to the questions which are included under the general title of chemical kinetics. This subject will be discussed in the second part of this work. At present I would warn the student against employing the term atom and molecule in a loose way, and at the same time remind him that unless we allow a certain degree of elasticity to our use of molecular and atomic conceptions, we cannot make much use of the measurements which have been so plentifully amassed by the aid of the calorimeter.

133. In the Introduction to volume I. of his *Essai de mécanique chimique*, Berthelot lays down three fundamental principles of thermal chemistry [p. xxviii—xxix].

(1) The quantity of heat evolved in a reaction measures the sum of the physical and chemical changes which occur in that reaction.

(2) The total thermal value of a reaction is dependent only on the initial and final states of the changing system.

(3) Every chemical change accomplished without addition of energy from without, tends to the formation of that body or system of bodies the production of which is accompanied by the evolution of the maximum quantity of heat.

The first and second principles have already been illustrated and discussed. The third, under the name of the "law of maximum work" forms the basis of all Berthelot's thermochemical generalisations. It is stated in an even more rigid form as the *theorem of the necessity of reactions*<sup>1</sup>, "Every chemical change which can be accomplished without the aid of a preliminary action or the addition of energy from without the system, necessarily occurs if it is accompanied by disengagement of heat."

This so-called *law of maximum work* cannot be fully discussed without introducing facts and considerations belonging to the domain of chemical kinetics<sup>2</sup>; but I think that if

<sup>1</sup> *loc. cit.* ; Introduction, p. xxix., also 2. 422.

<sup>2</sup> See *post*, Book II. chapter III. par. 241.

the fundamental distinction between atom and molecule is clearly grasped, it will at once be seen that Berthelot's statement is too general to be of much service in elucidating the mechanism of chemical change.

Berthelot's law is simply a crude application of the principle of the degradation of energy; the principle, namely, that energy always tends to run down from a more available to a less available form. Inasmuch as the production of a chemical compound, with evolution of heat, is an instance of such running down of energy, from the form of chemical affinity to that of heat, it follows that the reversal of this process will require the expenditure of work. But the *law of maximum work* does not attempt to analyse the expression *chemical affinity*. Under this term Berthelot includes actions and reactions of different kinds. This is at once apparent from the statement in the *Essai*<sup>1</sup>, that the first fundamental principle of thermal chemistry, viz.—“the quantity of heat evolved in a reaction measures the sum of the physical and chemical changes which occur in that reaction”—furnishes the measure of chemical affinities<sup>2</sup>.

Berthelot's work is saturated with the conceptions of the molecular theory: but, by some fatal perverseness, he refuses to apply this theory to chemical phenomena. While recognising the existence of molecules, and building his generalisation on a molecular foundation, he refuses to accept the conception of atom, or rather he hopelessly confuses it with that of equivalent. The molecule is for him a definite and definable portion of matter, the parts of the molecule are only numbers.

If by chemical affinity is meant an action and reaction between atoms, then the principle already quoted certainly does not afford a measure of this affinity.

Berthelot's law, then, appears to be a definite statement applicable to chemical reactions; but more precise investigation shews that the application is only possible when 'chemical' is used in a vague way as including much that is usually called 'physical.'

<sup>1</sup> Introduction, p. xxviii.

<sup>2</sup> 'Ce principe fournit la mesure des affinités chimiques.'

The principle of the degradation of energy is a highly generalised statement applicable to certain cycles of change; Berthelot attempts to apply it to parts of such cycles, forgetting that what is true of the whole is not necessarily true of the parts.

Thirty years ago Thomsen<sup>1</sup> generalised the relations between chemical action and thermal change in the statement, "Every simple or complex reaction of a purely chemical kind is accompanied by evolution of heat."

If by a reaction 'of a purely chemical kind' is meant the combination of atoms to form molecules, no objection can be made to this statement; we recognise its importance and universality, as we recognise the same qualities in such statements as 'all men are mortal,' or 'no white men are black.' But we may doubt its utility. Thomsen explains that 'reactions of a purely chemical kind' are those, which proceed without addition of energy from sources external to the system, and consist only of the strivings of atoms towards some stable equilibrium<sup>2</sup>. On the other hand a chemical system may be raised to a temperature such that its constituents are no longer stable, and reactions may then occur with expenditure of external energy; but these changes do not depend solely on mutual atomic attractions. But actions 'of a purely chemical kind' never occur, except as parts of cycles of reactions, which include changes that do not consist 'solely of the strivings of atoms towards more stable equilibrium.' Hydrogen and oxygen do not combine to form water, neither do chlorine and hydrogen combine to form hydrochloric acid, without the addition of energy from external sources.

Statements such as those quoted from Thomsen or Berthelot are true, only when an arbitrary separation is made of chemical changes into two parts, and one of these parts is

<sup>1</sup> See *Thermochemische Untersuchungen*, 1. 12—16.

<sup>2</sup> *loc. cit.* 1. 16.

<sup>3</sup> "Der chemische Process ist rein chemischer Natur, wenn er ohne Aufwand fremder Energie verläuft, und nur durch das Streben der Atome nach mehr stabilen Gleichgewichtslagen zu Stande kommt."



alone called chemical. Every chemical change, however simple, consists of at least two parts, the first of which is the necessary antecedent of the second; the *law of maximum work* ignores this duality, or, it might be more accurate to say, the law assumes that the second part of a chemical process can occur without the first. Every process of chemical change may be compared to the flight of a stone from, and its return to the surface of the earth. During the first part of this process there is a continual transference of kinetic energy from the moving stone to the surrounding medium, and during the second part, a continual transference from the medium to the stone, until the stone comes to rest, when its energy becomes a part of the total energy of the system, earth + stone. If the final resting-place of the stone is nearer the centre of the earth than the spot from which it was projected on its upward flight, then the stone contains less energy, relatively to surrounding systems, at the close of the transaction than at the beginning. On the other hand, if the starting-point is nearer the earth's centre than the final point of rest, then the transaction has resulted in gain of energy to the stone. In both cases the second part of the transaction, that which occurs between the turning-point and the final resting-point of the stone, is attended with loss of energy; but this second part does not represent the complete transaction. The *law of maximum work* is applicable only to the second part. And moreover this law ignores the fact that the stone (or chemical system) does not leave its initial point of rest of its own accord; the law assumes that no work need be done, no energy expended, in the passage of the (stone or system) from its original position to that at which the energy-relations between it and surrounding systems come within the cognisance of the law.

134. An attempt has been made by Thomsen to measure the thermal values of the first parts, i.e. separation of molecules into atoms, of certain changes which result in the production of hydrocarbons. Attention has already<sup>1</sup> been drawn to this investigation.

<sup>1</sup> See *ante*, chapter II. section IV. par. 84.

Thomsen's results are obtained by the aid of many hypotheses, some of which appear to be quite unjustified by facts<sup>1</sup>. Among such hypotheses I would place;—

(1) The assumption that the molecule of carbon is diatomic:

(2) The assumptions on which the reasoning is based whereby the thermal value of the process resulting in the formation of this diatomic molecule from amorphous carbon is calculated.

Thus, comparing the reactions

(a)  $C_2H_2 + H_2 = C_2H_4$ , (b)  $C_2H_4 + H_2 = C_2H_6$ , (c)  $C_2H_6 + H_2 = 2CH_4$ , it is found (assuming  $2CH_4$  to be equal to  $C_2H_6$ ) that the mean thermal value for the addition of  $H_2 = 14570$  gram-units.

But, at the same time the value of the reaction  $[C^2H^4, H^2]$  is found to be equal to  $[C^2H^2, H^2] + (2 \times 14,570)$ , and the value of the reaction  $[C^2H^2, H^2]$  is found to be equal to  $[C^2, H^2] + (3 \times 14,570)$ .

Hence, if we assume that the value of the reaction  $[C^2, H^2]$  is equal to  $[C, C] + (4 \times 14,570)$ , it follows from the known value of the reaction  $[C^2, H^2]$ , that  $[C, C] = 106,630$  units<sup>2</sup>.

But this value  $[C, C]$  represents the sum of two thermal changes, (a) the heat absorbed in gasifying amorphous carbon and separating the molecule into its pair of constituent atoms, and (b) the heat evolved in the falling together of a pair of atoms to form the (hypothetical) diatomic gaseous molecule  $C_2$ . Thomsen attempts to determine the value of (a); but in doing this he makes another startling assumption *viz.*

that because  $[C, O^2] = 96,960$ , and  $[CO, O] = 68,080$ ,  
therefore  $[C, O] = [C, O^2] - [CO, O] = 28,880$ .

<sup>1</sup> Thomsen's papers will be found in *Ber.* 13. 1321 and 1388; and 15. 318 (also *Journal für prakt. Chemie.* 131. 157). A much condensed account is given in Thomsen's *Thermochemische Untersuchungen*, 2. 96—113. A clear and full account of Thomsen's investigation, by J. P. Cooke, appeared in *Amer. Journal of Science and Arts* [3], 21. 87—98.

<sup>2</sup> Thomsen uses this value to calculate the reaction  $[C^2, H^2]$ ,  $[C^2H^2, H^2]$  &c., but of course the results agree with those actually found by experiment.

Thomsen apparently forgets that the reaction  $[C, O^*]$  represents the production of 44 grams of gaseous carbonic anhydride from 32 grams of gaseous oxygen and 12 grams of solid carbon; whereas the reaction  $[CO, O]$  represents the addition of 16 grams of gaseous oxygen to 28 grams of gaseous carbon monoxide<sup>1</sup>.

Some very strange results are obtained by Thomsen: e.g. he thinks it very probable that  $[O, C, O] = 2 [C, O]$ , but the numbers on which his own hypothesis is based shew that  $[O, C, O] - 2 [C, O] = 39,200 +$ ; in fact this value is constantly used throughout the investigation. Again the calculated probable value of the heat absorbed in separating two carbon atoms from amorphous carbon is 77,800 units, but to do this, and also to form the diatomic molecule  $C_2$  from these separated atoms, requires an absorption of 106,630 units, therefore the falling together of two carbon atoms to form a molecule is attended with the *absorption* of 28,830 units of heat.

Later on we find that the strange behaviour of the atoms of carbon is to be traced to the vagaries of their 'bonds.' Two atoms of carbon may unite, on the bond hypothesis, in four ways:—

- (1) One bond of each atom is satisfied by one bond of the other atom :  
heat *evolution* = about 14,500 units.
- (2) Two bonds of each atom are satisfied by two bonds of the other atom :  
heat *evolution* = 14,500 units.
- (3) Three bonds of each atom are satisfied by three bonds of the other atom : heat *evolution* = 0.
- (4) Four bonds of each atom are satisfied by four bonds of the other atom : heat *absorption* = about 28,000 units.

It also follows from Thomsen's numbers that  $[C, C] < [C, H]$ , and that  $[C, O] > [C, C]$  (when  $C + C$  forms  $C - C$ ).

As might be expected, the application by Thomsen of his hypothetically determined values leads to somewhat anomalous results. The calculated heats of formation of hydrocarbons sometimes agree fairly well with the observed numbers, sometimes there are marked differences between the two

<sup>1</sup> See also *ante*, this section, par. 130.

numbers. Thus, comparing the observed and calculated heats of combustion (because these are the bases for calculating heats of formation) of benzene and dipropargyl, we have this result.

### I. HEAT OF COMBUSTION OF BENZENE ( $C_6H_6$ ).

*On the assumption that each carbon atom is trivalent (or, that the molecule contains 3 'double bonds' and 3 'single bonds' between carbon atoms).*

*On the assumption that each carbon atom is tetravalent (or, that the molecule contains 9 'single bonds' between carbon atoms).*

Calculated.	Difference.	Observed.	Calculated.	Difference.	Observed.
844,500	- 38,700	805,800 (1)	800,400	+ 5,400	805,800 (1)
844,500	- 56,500	788,000 (2)	800,400	- 12,400	788,000 (2)

(1) Earlier, (2) later observations.

### II. HEAT OF COMBUSTION OF BENZENE AND DIPROPARGYL ( $C_6H_6$ ).

Berthelot's numbers.

*Observed Difference.*

Thomsen's numbers.

dipropargyl = 853,600  
benzene = 776,000

> 77,600 - ..... 95,200 -

< 883,200 = dipropargyl  
< 788,000 = benzene

*Calculated difference*, (1) on the assumption that each carbon atom in the benzene molecule is tetravalent = 88,200.

*Calculated difference* (2) on the assumption that each carbon atom in the benzene molecule is trivalent = 44,100.

The numbers representing the heats of combustion of dipropargyl and benzene obtained by Berthelot, are considerably greater than those obtained by Thomsen; the difference amounts, in the former case, to 29,600, and in the latter case to 12,000 units.

It would evidently be absurd to draw any precise conclusions regarding the structure of the molecules of benzene and dipropargyl from these results<sup>1</sup>.

Two general conclusions may, I think, be drawn from Thomsen's investigation; (1) that the energy-changes attending the formation of isomeric molecules are correlated, not only with the valencies of the constituent atoms, but also with the distribution of the atomic interactions<sup>2</sup>; (2) that the use of

<sup>1</sup> For a criticism of Thomsen's conclusions regarding the structure of hydrocarbons see Mendeleeff, *Ber.* 15. 1555; or *C. S. Journal, Abstracts* for 1882, 916.

<sup>2</sup> Lothar Meyer, *Die Modernen Theorien der Chemie*, 424, puts the conclusion to be drawn regarding the 'linking' of two carbon atoms thus, "what we call

that nomenclature which is founded on the hypothesis of bonds ought to be abandoned<sup>1</sup>.

135. A few generalisations have been established regarding the connection between the structure and the boiling point of carbon compounds. Thus the difference between the boiling points of two consecutive members of an homologous series of carbon compounds is frequently about 19°: but the numbers actually obtained shew that variations in the boiling points are connected with variations other than those of molecular weight. Goldstein<sup>2</sup> attempts to shew that the proportion between the numbers of hydrogen and carbon atoms, besides the total number of these atoms, influences the boiling points of the members of an homologous series. Hydrocarbons of analogous constitution must be compared, i.e. normal hydrocarbons must be compared with normal,

e.g.  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_3$  with  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ; or iso-with iso-hydrocarbons, e.g.

$\text{CH}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_3$  with  $\text{CH}(\text{CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ; nor can the differences between the boiling points of normal, be compared with the differences between the boiling points of iso-hydrocarbons.

Goldstein investigates the change of boiling point in the series of normal paraffins: i.e. hydrocarbons of the form  $\text{CH}_3-(\text{CH}_2)_x-\text{CH}_3$  [or  $\text{CH}_3-\text{CHR}'-\text{CH}_3$ ]. He gives the formula

$$\text{B. P.} = \text{b. p.} + \left(19 + \frac{380}{n(n+1)}\right),$$

where B. P. = boiling point required, b. p. = boiling point of the paraffin containing  $\text{CH}_3$  less than that whose B. P. is required, and  $n$  = number of atoms of carbon in the molecule of the paraffin whose B. P. is known. Thus, the boiling point of  $\text{C}_5\text{H}_{12}$  (i.e.  $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ ) is 39°; required the boiling point of  $\text{C}_6\text{H}_{14}$  (i.e.  $\text{CH}_3(\text{CH}_2)_4\text{CH}_3$ ).

double, or triple, linking of atoms, does not consist of a repetition of the process which we call single linking."

<sup>1</sup> See *ante*, chapter II. section IV. par. 84.

<sup>2</sup> *Ber.* 12. 689; also abstract of paper in Russian, *C. S. Journal Abstracts* for 1882, 374.

$$\begin{aligned}
 \text{B.P. required} &= 39 + \left( 19 + \frac{380}{n(n+1)} \right) \\
 &= 39 + 19 + \frac{380}{30} \\
 &= 39 + 19 + 12.66 \\
 &= 70.66.
 \end{aligned}$$

B.P. observed = 70.6.

Goldstein calculated the B. P. of normal heptane ( $C_7H_{16}$ ) to be 98.65; shortly after this, the paraffin was obtained in quantity by Thorpe, and the boiling point was found to be 98.5.

The same formula appears to hold good for determining the difference between the boiling points of any two consecutive iso-paraffins belonging to the form  $CH(CH_3)_4 - (CH_2)_n - CH_3$ . Thus,

B.P. Difference.

$$\begin{aligned}
 (a) \text{ } CH(CH_3)_2 - CH_2 - CH_3 & \quad 30.5 \\
 (b) \text{ } CH(CH_3)_2 - (CH_2)_2 - CH_3 & \quad 62.0
 \end{aligned}
 > 31.5 \dots \text{calculated difference} = 31.66.$$

If this is so, it follows that the difference between the boiling point of a normal – and its corresponding iso-paraffin (of this form) must be the same whatever be the molecular weight of the two isomerides. Experiment, so far as it has gone, seems to confirm this result; thus,

Formula.	Difference between B.P. of normal and iso-paraffin.
$C_5H_{12}$	8.5
$C_6H_{14}$	8.6
$C_7H_{16}$	8.5

Kahlbaum<sup>1</sup> has made some determinations of the ratio between the change in the boiling points of ethylic alcohols and acetic acids, and the diminution of pressure, and has concluded that a definite relation exists between at least the empirical formula of a compound and the ratio in question.

We have very little precise knowledge regarding the boiling points of isomeric hydrocarbons. From the data accumulated it has been concluded, that, of two or more isomeric hydrocarbons, that one has the lowest boiling point, the molecule of which is characterised by containing the greatest number of 'side chains'. Thus

<sup>1</sup> Ber. 16. 2476; 17. 1245, and 1263.

<sup>2</sup> For data see Naumann, *loc. cit.* pp. 168–172.

<i>Pentane</i> ( $C_5H_{12}$ ).		B.P.
(a) normal :— $CH_3(CH_2)_3-CH_3$		39°
(b) isopropyl-methylmethane :— $CH_3-CH(CH_3)_2-CH_3$		30°·5
(c) tetramethylmethane :— $C(CH_3)_4$		9°·5

<i>Hexane</i> ( $C_6H_{14}$ ).		
(a) normal :— $CH_3(CH_2)_4CH_3$		70°·5
(b) isopropyl-ethylmethane :— $CH_3-CH(CH_3)_2-C_2H_5$		62°
(c) di-isopropyl :— $CH(CH_3)_2-CH(CH_3)_2$		58°
(d) trimethyl-ethylmethane :— $C(CH_3)_3(C_2H_5)$		43°—48°

136. In this section I have tried to trace some of the connections between the results of thermal measurements of chemical phenomena and the statical aspects of these phenomena. We have found that every chemical phenomenon is a complex occurrence, and that it is almost impossible fully to differentiate those portions which would more appropriately be called physical, from those which are undoubtedly chemical. We have also found that thermal measurements, being essentially measurements of changes of energy, are intimately connected with problems belonging to chemical kinetics, and that until we have some precise knowledge regarding chemical affinity we are not in a position fully to discuss the data of thermal chemistry.

## SECTION II. *Optical Methods.*

137. In this section I wish to give some account of the attempts which have been made to elucidate the relations existing between (1) the refractive powers, (2) the power of rotating a ray of polarised light, and (3) the absorption spectra, and the composition of certain chemical compounds. The subject is more limited than that considered in the first section of the present chapter; it belongs, more completely than thermal chemistry, to the domain of chemical statics, although like other questions in chemical science, it is under certain aspects best considered from a kinetical point of view.

138. Let a ray of light pass from air into a liquid medium denser than air; let the angle of incidence =  $i$ , and the angle

of refraction =  $r$ ; then  $\frac{\sin i}{\sin r} = \mu$  = refractive index of the medium.

Let the light employed consist only of light of one wave-length, and let the liquid medium consist of a single definite chemical compound, then the quantity  $\left(\frac{\mu - 1}{d}\right)$  was called by Gladstone and Dale<sup>1</sup> the *specific refractive energy* of the liquid examined, ( $d$  = density of the liquid referred to water as unity). Landolt<sup>2</sup> called the product obtained by multiplying  $\left(\frac{\mu - 1}{d}\right)$  into the molecular weight of the liquid, i.e.  $\left(\frac{\mu - 1}{d}\right)M$ , the *refraction equivalent* of the liquid compound in question.

The quantity  $\left(\frac{\mu - 1}{d}\right)$  was said by Gladstone and Dale to be independent of temperature<sup>3</sup>.

The refraction-equivalent of the molecule of a chemical compound is generally said to be the sum of the refraction-equivalents of the atoms which compose the molecule: or the refraction-equivalent of a mixture is the sum of the equivalents of its components<sup>4</sup>.

But objection has been taken by Wiedemann<sup>5</sup> to the use of the constant  $\left(\frac{\mu - 1}{d}\right)M$  in attempts to trace connections between the composition and the optical properties of compounds. Any relations which appear to exist between molecular composition and physical properties must, it is urged, be formal rather than real relations, as long as the properties of the molecule are assumed to be the sum of the properties of the atoms. Physical constants ought to be employed which determine the properties of atoms.

<sup>1</sup> *Proc. R. S.* 12. 448, and *Phil. Trans.* 153. 317.

<sup>2</sup> *Pogg. Ann.* 122. 545; and 123. 595.

<sup>3</sup> See *Proc. R. S.* 18. 49; and also *Phil. Trans.* 160. 9.

<sup>4</sup> See especially Landolt, *Pogg. Ann.* 123. 623.

<sup>5</sup> *Ber.* 15. 467.



Now A. Lorenz and H. Lorenz<sup>1</sup>, within the last few years, independently deduced the expression

$$\frac{\mu^2 - 1}{(\mu^2 + 2)d} = c$$

from the general principles of the undulatory theory of light (and more especially from Maxwell's electromagnetic theory), as giving a statement of the relation between the velocity of transmission of light, and the density of the liquid medium through which it is propagated.

Landolt<sup>2</sup> has applied the two formulæ

$$(1) \left( \frac{\mu - 1}{d} \right) M, \quad (2) \left( \frac{\mu^2 - 1}{(\mu^2 + 2)d} \right) M,$$

to calculate the refraction-equivalents of mixtures, on the supposition that these equivalents are equal to the sums of the equivalents of the constituents, and has found that the results are the same whichever formula is adopted; and moreover that the observed agree with the calculated results, except when very strongly refractive liquids, such as carbon disulphide, are employed. Hence Landolt argues that conclusions regarding the connection between the molecular composition and the refraction-equivalents of compounds, deduced by aid of the first (purely empirical) formula, are confirmed by the use of the second formula, which is deduced from the general principles of the undulatory theory of light.

But neither formula is independent of dispersion. It is however possible by the use of Cauchy's formula to arrive at an expression for the refraction-equivalent which is practically independent of dispersion<sup>3</sup>. This expression may be formulated as

$$\left( \frac{A\mu - 1}{d} \right) M, \quad \text{or} \quad \left( \frac{A^2\mu - 1}{(A^2\mu + 2)d} \right) M,$$

<sup>1</sup> *Wied. Ann.* 9. 641; and 11. 70.

<sup>2</sup> *Ber.* 15. 1031.

<sup>3</sup> For details consult a text-book on Optics (e.g. see Glazebrook's *Physical Optics*, pp. 244—46). But it appears, from an investigation by Langley, that this formula gives erroneous results 'when extended far beyond the limits within which the observations on which it is founded are made.' See *Phil. Mag.* for March 1884; or in full, *Ann. Phys. Chim.* (6) 2. 145. Hence, the apparently anomalous refraction-equivalents of some carbon compounds (see *post.*, par. 142) may be due to the very great dispersion which is noticed in these cases. See Gladstone, *C. S. Journal. Trans.* for 1884. 241.

where  $A_\mu$  = refractive index of the theoretical ray of infinite wave-length.

We have then the four expressions for finding the refraction-equivalent of a liquid compound ;

$$\begin{aligned} (1)^1 \left( \frac{\mu_a - 1}{d} \right) M &= (R_a) & (2) \left( \frac{A_\mu - 1}{d} \right) M &= (R_A) \\ (3)^1 \left( \frac{\mu_a^2 - 1}{(\mu_a^2 + 2)d} \right) M &= (R_a) & (4) \left( \frac{A_\mu^2 - 1}{(A_\mu^2 + 2)d} \right) M &= (R_A) \end{aligned}$$

The values obtained by equations (3) and (4) are about one-third less than those obtained by the use of equations (1) and (2).

These formulæ yield expressions for finding the refraction-equivalent of each constituent of a mixture, or that of each atom in the molecule of a liquid compound, if it is assumed that the equivalent of the mixture, or of the molecule, is the sum of the equivalents of the constituents of the mixture, or of the atoms which constitute the molecule<sup>2</sup>. The 'atomic refraction' of an element, deduced by each equation (1) to (4), may be represented by the symbols (1)  $r_a$ , (2)  $r_A$ , (3)  $r_a$ , (4)  $r_A$  respectively.

139. Is the value of  $r_A$ , or  $r_a$ , constant for each element in all its liquid compounds?

This question has been considered by Gladstone and Dale (*loc. cit.*)<sup>3</sup>, and by Landolt (*loc. cit.*)<sup>4</sup>, but more especially by Brühl<sup>5</sup>.

Assuming that the refraction-equivalent of each elementary atom has a constant value in all compounds of that element, and that the equivalent of a molecule is the sum of the equivalents of the constituent atoms, we have the expression for finding the refraction-equivalent of a compound,  $C_n H_{2m} O_p$ ,

$$(R_A) = n \cdot r_A C + 2m \cdot r_A H + p \cdot r_A O :$$

<sup>1</sup> Light with wave-length of the red hydrogen line  $H\alpha$  is usually employed for determining  $\mu$ .

<sup>2</sup> See Landolt, *Ber.* 18. 1033.

<sup>3</sup> See also, Gladstone, *C. S. Journal. Trans.* for 1884. 241.

<sup>4</sup> See also *Pogg.* 117. 353. and *Annalen, Supplbd.* 4. 1.

<sup>5</sup> *Ber.* 12. 2135 : 13. 1119 and 1520 : 14. 2533, 2736 and 2797 ; also (in more detail) in *Annalen* 200. 139 : 203. 1, 255, and 363 : 211. 120 (Abstracts in *C. S. Journal* for 1880. 293 and 781 : 1881. 15 : 1882. 445).

and similarly for compounds of other elements. From the application of such expressions, Landolt, and others, deduced the following values ;

$r_A$  for H=1.29 ; for O=2.71 ; for C=4.86 ; for S=13.53 ; for Cl=9.53.

Or, if equation (4) [p. 309] is employed, then

$r_A$  for H=1.02 ; for O=1.56 ; for C=2.43 ; for S=7.65 ; for Cl=5.89.

The values of ( $R_A$ ), thus calculated, for many liquid carbon compounds, were found to agree with the observed values. Thus, the refraction-equivalents of pairs of carbon compounds differing in composition only by  $H_2$  should differ by  $2.129 = 2.58$  ; the following are some of the differences observed,

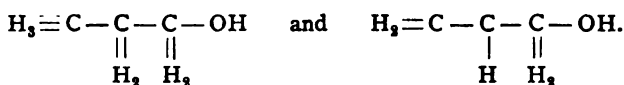
$(R_A)C_2H_6O - (R_A)C_2H_4O = 2.14$  ;  $(R_A)C_3H_8O - (R_A)C_3H_6O = 2.45$  :

$(R_A)C_4H_{10}O - (R_A)C_4H_8O = 2.52$ , &c. &c.

But the following numbers shew that this generalisation does not always hold good ;

Difference of ( $R_A$ )			
Propylic alcohol	$C_3H_8O$	} 0.91	} 0.73 { Propylic chloride $C_3H_7Cl$
Allylic alcohol	$C_3H_6O$		
Propaldehyde	$C_3H_6O$	} 0.11	} Allylic chloride $C_3H_5Cl$
Acraldehyde	$C_3H_4O$		

The refraction-equivalent of the carbon, hydrogen, oxygen, or chlorine atom, or of all these atoms, is evidently not constant. Now, if the structural formulæ of propyl compounds are compared with those of allyl compounds, it is seen that in the former all the carbon atoms are represented as tetravalent (singly-linked), but in the latter two carbon atoms are represented as trivalent (doubly-linked) ; e.g.



Hence, the disagreement between the calculated and the observed values of ( $R_A$ ) in the case of allyl compounds may be correlated with the presence of trivalent (doubly-linked) carbon atoms in the molecules of these compounds. Moreover, the actual values of ( $R_A$ ) for propyl compounds agree

with those calculated by the equation on p. 309, taking  $r_A$  for  $C = 4.86$ , for  $H = 1.29$  and for  $O = 2.71$ ; but the values found for allyl compounds are about 2 units greater than the calculated values. Thus,

	Difference between calculated and observed ( $R_A$ )	
	+	
Allyl alcohol	1.87	} mean = 2.10.
„ aldehyde	2.67	
„ chloride	2.07	
Allyl-ethyl oxide	2.10	
„ acetate	1.79	

Brühl has compared the values of ( $R_A$ ) for a great many pairs of carbon compounds, one series containing only tetravalent, the other also trivalent carbon atoms, and has found that the observed agree with the calculated values in the first series, but in the second the observed values are about 2 units greater than the calculated values, for each pair of trivalent carbon atoms in the molecule<sup>1</sup>.

This conclusion may be summarised by saying, that two values are to be assigned to the refraction-equivalent of the carbon atom, according as it acts as a tetravalent (singly-linked), or trivalent (doubly-linked) atom. The values are these,

$$r_A C^{IV} = 4.86 : r_{\Delta} C^{IV} = 2.43$$

$$r_A C^{III} = 5.86 : r_{\Delta} C^{III} = 3.22$$

Further, Brühl has compared series of compounds containing tetravalent carbon, and divalent oxygen atoms, with series containing tetravalent carbon, and monovalent (doubly-linked) oxygen atoms, and he has found that the value of ( $R_A$ ) for any compound of the second series is about 0.6 greater (for each monovalent oxygen atom) than that for the compound of the first series having the same empirical formula<sup>2</sup>.

We may then assign these values to the atoms of oxygen :

$$r_A O^{II} = 2.71 \quad r_{\Delta} O^{II} = 1.56$$

$$r_A O^I = 3.29 \quad r_{\Delta} O^I = 2.29.$$

Hence it would appear that the influence exerted on the refraction-equivalent of a liquid carbon compound by the

<sup>1</sup> See numbers in *Ber.* 12. 2142.

<sup>2</sup> See numbers in *Ber.* 13. 1121.

atoms of carbon in the molecule, depends on whether each carbon atom acts on, and is acted on by, four or three other atoms.

140. But does this influence vary in accordance with the nature of the atoms, between which and the carbon atoms there is direct mutual action?

Brühl<sup>1</sup> finds that each of the following groups of isomeric compounds of carbon, hydrogen, and oxygen has practically the same refraction-equivalent.

I.	(R <sub>a</sub> )	II.	(R <sub>a</sub> )
$\text{ClH}_2\text{C}-\text{CH}_2\text{Cl}$ and $\text{Cl}_2\text{HC}-\text{CH}_3$	} 34.9	$\begin{array}{c} \text{H} \\   \\ \text{H}_3\text{C}-\text{C}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{H} \end{array} \\   \\ \text{H} \end{array}$	} 26.0
$\text{H}_2\text{C}-\text{CH}_2-\text{CH}_3$   OH and $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{HC} \\   \\ \text{CH}_2 \\   \\ \text{OH} \end{array}$		$\text{H}_3\text{C}-\text{C}-\text{CH}_3$   O	
$\text{H}_2\text{C}-\text{CH}_2-\text{CH}_3$   Br	} 28.6	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{H} \end{array} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	} 36.7
and $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{HC} \\   \\ \text{CH}_3 \\   \\ \text{Br} \end{array}$		$\text{H}_3\text{C}-\text{C}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{H} \end{array}$   H	
$\text{H}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$   OH	} 39.4	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}_3\text{C}-\text{C}-\text{C}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OH} \end{array} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	} 36.3
and $\text{H}_2\text{C}-\text{CH} \begin{array}{l} \diagup \text{CH}_3 \\ \diagdown \text{CH}_3 \end{array}$   OH		$\text{H}_3\text{C}-\text{C}-\text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{OH} \end{array}$   H	
and $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}-\text{CH}_3 \\   \\ \text{CH}_3 \\   \\ \text{OH} \end{array}$	} 36.3		

<sup>1</sup> See *Ber.* 13, 1521.

The molecules of the compounds placed in column I. contain only tetravalent carbon, and divalent oxygen atoms; those in column II. contain both tetra- and tri-valent carbon, and di- and monovalent oxygen atoms.

Brühl also finds<sup>1</sup> that although the refraction-equivalent of propaldelyde is the same as that of acetone, yet that of the third isomeride, allylic alcohol, is different; thus,

*Empirical formula*  $C_3H_6O$ .

		( $R_d$ )
1. Propaldehyde	$  \begin{array}{c}  H \\    \\  H_3C-C-C \begin{array}{l} \nearrow O \\ \searrow H \end{array} \\    \\  H  \end{array}  $	26°0
2. Acetone	$  \begin{array}{c}  H_3C-C-CH_3 \\    \\  O  \end{array}  $	26°0
3. Allylic alcohol	$  \begin{array}{c}  H_3C-C-C \begin{array}{l} \nearrow H_2 \\ \searrow OH \end{array} \\    \\  H  \end{array}  $	27°90

A comparison of these formulæ shews, that whereas in isomerides 1 and 2 the trivalent carbon atom is in direct union with an oxygen and a carbon atom, in the third isomeride it is directly bound only to carbon atoms: or we may say that isomerides 1 and 2 contain a divalent group C—O, whereas isomeride 3 contains a tetravalent group C—C, and a trivalent C—O group.

If we may draw a general conclusion from the data contained in Brühl's paper, it would seem that the value of the refraction-equivalent of a compound,  $C_xO_yH_z$ , is independent of the way in which the interatomic reactions are distributed, provided each atom acts on its maximum number of other atoms; but if this is not so, then there is a connection, not only between the valencies of the atoms in the molecule, but also between the distribution of the interatomic reactions, and the refraction-equivalent.

The latter part of this statement is illustrated by the fact that the value of ( $R_d$ ) found for  $(CH_3)_2CO$ , and for the acids

<sup>1</sup> *loc. cit.*

$C_nH_{2n+1}COOH$ , which all contain the divalent group  $C=O$ , agrees with that calculated on the assumption that

$$\begin{aligned}(R_A)(C=O)^{II} &= r_A C^{II} + r_A O^I \\ &= 4.86 + 3.29 \\ &= 8.15;\end{aligned}$$

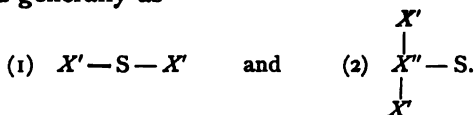
but nevertheless the carbon atom in the group  $C=O$ , as this occurs in the before-mentioned molecules, is certainly trivalent.

On the other hand the actual values found for  $(R_A)$  in the molecules  $C_nH_{2n-1}CH_2OH$ ,  $C_nH_{2n}$ , &c., where the tetravalent group  $C=C$  occurs, agree with those calculated on the assumption that

$$\begin{aligned}(R_A)(C=C)^{IV} &= 2(r_A C^{III}) \\ &= 11.72.\end{aligned}$$

That there is a distinct quantitative connection between the nature of the polyvalent atoms between which direct action and reaction occurs, in unsaturated molecules, and the value of  $(R_A)$  for these molecules, appears certain from the results of researches recently conducted in Landolt's laboratory by Nasini<sup>1</sup>.

Nasini has determined the values of  $(R_A)$  and  $(R_\Delta)$ , for series of carbon compounds containing sulphur, these compounds being divisible into two groups<sup>2</sup>, which may be represented generally as



He gets the following values for the refraction-equivalent of the sulphur atom according as it acts as a divalent or as a monovalent atom,

$$\begin{array}{ll} r_A S^{II} = 13.53 & r_\Delta S^{II} = 7.65 \\ r_A S^I = 15.09 & r_\Delta S^I = 8.84. \end{array}$$

<sup>1</sup> Ber. 15. 2878.

<sup>2</sup> As examples of compounds belonging to group (1) may be taken,  $H_5C_2-S-H$ , and  $H_5C_2-S-C_2H_5$ ; also  $\begin{array}{c} \diagup S-C_2H_5 \\ CO \\ \diagdown S-C_2H_5 \end{array}$  and  $\begin{array}{c} \diagup O-C_2H_5 \\ CO \\ \diagdown S-C_2H_5 \end{array}$ ; and as examples of those belonging to group (2),  $\begin{array}{c} S \\ \diagup C \\ \diagdown S \end{array}$ ,  $\begin{array}{c} O-C_2H_5 \\ \diagup C-S \\ \diagdown O-C_2H_5 \end{array}$  &c.

Wiedemann<sup>1</sup> has also determined values for  $r_A S$ , from measurements of ( $R_A$ ) of  $\text{CO}(\text{OEt})_2$ ,  $\text{CO}(\text{OEt})(\text{SEt})$ ,  $\text{CS}(\text{OEt})_2$ ,  $\text{CS}(\text{OEt})(\text{SEt})$ ,  $\text{CO}(\text{SEt})_2$ , and  $\text{CS}(\text{SEt})_2$ . The values agree fairly with those found by Nasini; they are as follows,

$$r_A S^{\text{II}} = 14.04$$

$$r_{\Delta} S^{\text{II}} = 7.94$$

$$r_A S^{\text{I}} = 16.32$$

$$r_{\Delta} S^{\text{I}} = 9.28.$$

But when it is sought to find values for  $r_A S$  in more complex compounds containing oxygen, very different results are obtained according to the structure assigned to the compound molecules in question. Thus, assuming that  $r_A \text{O}^{\text{I}} = 3.29$ , and  $r_A \text{O}^{\text{II}} = 2.71$ , the following results are obtained<sup>2</sup>.

$$(1) \text{ If } \text{SO}_2 = \text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}, r_A S^{\text{II}} = 8.10; \text{ but if } \text{SO}_2 = \text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}, r_A S^{\text{II}} = 6.94.$$

$$(2) \text{ If } \text{SO}_3 = \text{O} - \text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array}, r_A S^{\text{III}} = 8.37; \text{ but if } \text{SO}_3 = \text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} - \text{O}, r_A S^{\text{III}} = 6.63.$$

$$(3) \text{ If } \text{H}_2\text{SO}_4 = \text{HO} - \text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} - \text{O} - \text{OH}, r_A S^{\text{III}} = 8.43.$$

$$(4) \text{ If } \text{H}_2\text{SO}_4 = \text{HO} - \text{S} \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{array} - \text{OH}, r_A S^{\text{IV}} = 7.85.$$

I think we are justified in concluding that the refraction-equivalents of molecules containing polyvalent atoms, all, or any, of which act directly on less than their maximum number of other atoms, is correlated not only with the actual valencies of these atoms (i.e. the number of atoms between which and each polyvalent atom there is direct mutual action), but also with the distribution of the interatomic actions (i.e. the nature of the atoms between which there is direct mutual action)<sup>3</sup>.

The quantity ( $R_A$ ) is conditioned by these factors, refractive index ( $\mu$ ), density ( $d$ ), and molecular weight ( $M$ ). The values of  $\mu$  and  $d$  vary for each compound: when  $d$  varies directly as  $\mu$ , the value of ( $R_A$ ) remains constant for

<sup>1</sup> *Wied. Ann.* 17. 577.

<sup>2</sup> For data see Nasini *loc. cit.*

<sup>3</sup> This conclusion, if accurate, illustrates the justness of the remark already quoted from L. Meyer, "what we call double or triple linking of atoms does not consist of a repetition of the process which we call single linking."



any number of isomerides ; but if  $d$  varies in some other ratio with  $\mu$ , the value of  $(R_A)$  is different for each isomeride. The latter condition holds good in such unsaturated molecules as have been just defined. But in many saturated molecules, according to Brühl, the former state of things obtains ; hence, although the refraction-equivalent of such molecules is constant, yet their refractive indices vary. This conclusion may be put in general terms thus. Isomeric molecules containing polyvalent atoms, all of which act on their maximum number of other atoms, exhibit equal refractive powers only when their densities are the same<sup>1</sup>.

141. Values have been assigned to the atomic refractions of the elements, (or the refraction-equivalents of the elementary atoms). Assuming that these values are justified by the experimental data, it is important to mark that in making use of them we do not assert that each atom in a molecule exerts its own refractive power, but rather that a group of certain atoms arranged in this or that manner, (as roughly represented in the structural formula), exerts a definite refractive power, which is increased or diminished by changes in the arrangement, number, or nature of the atoms.

It would appear better to assign values to the refraction-equivalents of certain groups of atoms, in carbon compounds at least, rather than to each individual atom. The following table contains some of these values, and also recapitulates the 'atomic refractions' which have already been mentioned.

	$r_A$	$r_B$
C <sup>IV</sup>	4.86	2.43
C <sup>III</sup>	5.86	3.22
(C—C) <sup>IV</sup>	11.72	6.44
(C—O) <sup>II</sup>	8.15	4.72
(CH <sub>2</sub> ) <sup>II</sup>	7.44	4.47
O <sup>II</sup>	2.71	1.56
O <sup>I</sup>	3.29	2.29
S <sup>II</sup>	13.53	7.65
S <sup>I</sup>	15.09	8.84
H	1.29	1.02
Cl	9.53	5.89.

<sup>1</sup> See Brühl, *Ber.* 18. 1525—26.

142. The refraction-equivalents of a few carbon compounds belonging to the benzenoid group have been determined<sup>1</sup>. The arrangement of carbon atoms in a closed chain does not appear to exert any special influence on the values of the constant in question; thus ( $R_d$ ) found for benzene, agrees with that calculated on the assumption that the six atoms of carbon all act as trivalent atoms in the molecule  $C_6H_6$ .

Few, if any, measurements have yet been made of the refraction-equivalents of carbon compounds containing pairs of divalent (trebly-linked) carbon atoms. Brühl<sup>2</sup> has determined ( $R_d$ ) for a few so-called propargyl compounds, derived from the hydrocarbon  $C_3H_4$ , which possibly has the structure  $H-C-C \equiv C-H$ .

Thus,

Probable formula.	$(R_d)$	
	found	calculated, on the assumption that $(R_d)(C-C)^{II}$ $= (R_d)(C-C)^{IV} = 11.72$
Propargylic alcohol $HC-C \begin{smallmatrix} \diagup H_2 \\ \diagdown OH \end{smallmatrix}$	24.01	24.45
Propargyl-ethyl oxide $HC-C \begin{smallmatrix} \diagup H_2 \\ \diagdown O \end{smallmatrix}$ $H_3C-CH_3$	39.50	39.33
Propargyl acetate $HC-C \begin{smallmatrix} \diagup H_2 \\ \diagdown O-C \begin{smallmatrix}   \\ O \end{smallmatrix} \end{smallmatrix}$ $H_3$	37.7	37.33

The refraction-equivalents of some compounds containing much carbon, relatively to the quantities of other elements present, are considerably larger than the values calculated by the use of the numbers given in par. 141<sup>3</sup>.

<sup>1</sup> See especially for data Landolt, *Ber.* 15. 1038; and Brühl, *Ber.* 12. 2142.

<sup>2</sup> *loc. cit.* 12. 2146.

<sup>3</sup> For data see Gladstone's paper, *C. S. Journal, Trans.* for 1884. 241. See also *ante*, par. 138, footnote 3 (p. 308).

143. We have not yet sufficient knowledge to enable us to use the refraction-equivalent of a compound, otherwise than very tentatively, as a help in deciding between the possible structural formulæ assigned to that compound. Brühl has employed the observed values of the constant ( $R_A$ ) as an argument in favour of, or against, certain formulæ, but not, it appears to me, with much success<sup>1</sup>.

From comparing the values of ( $R_A$ ) with the structural formulæ of certain carbon compounds, the same naturalist has drawn conclusions regarding the meanings of the symbolical expressions 'single' and 'double bonds'; but, as seems always the case in attempts to deal with 'bonds', the foundations of the reasoning are shifting, and the superstructure is untrustworthy<sup>2</sup>.

144. If a ray of plane polarised light is passed through a plate of quartz cut at right angles to its optical axis, the position of the plane of polarisation of the emergent ray does not coincide with that of the incident ray; the plane has been rotated through a certain angle, called the angle of rotation. If the rotation takes place in the same direction as that in

<sup>1</sup> See *Ber.* 12. 2146, and 14. 2736.

<sup>2</sup> See Book II. chap. IV. par. 258. Kanonnikow (original paper in Russian; see abstract in *Ber.* 16. 3047) has found the refraction-equivalents of a number of solid carbon compounds, by dissolving them in chemically inactive solvents, and measuring the refractive indices of the solutions, the values of the indices of the solvent being known; it is then easy to find the refraction-equivalent of the dissolved substance, if it be granted that the refraction-equivalent of a mixture is the sum of the equivalents of its components (see *ante*, p. 307-9). Kanonnikow concludes that neither the degree of concentration of the solution, nor the physical condition of the solid, exerts any marked effect on the refractive power of the dissolved substance.

Conclusions are drawn as to the structural formulæ of various carbon compounds; Brühl's generalisations, on the whole, are confirmed.

The same chemist (see abstract in *Ber.* 17. ref. 157. [the abstracts, *referate*, in the *Berichte* beginning with vol. 17 are paged separately from the original papers]) has attempted to determine  $r_A$  for various metals, by finding ( $R_A$ ) for various salts of carbon acids, and deducting ( $R_A$ ) for the acids. His numbers point to the conclusion that in a 'group' of metals (as 'group' is used in the classification based on the periodic law),  $r_A$  increases as the atomic weights of the metals increase. Kanonnikow also tries to deduce values for ( $R_A$ ) for the groups  $\text{NO}_3$ ,  $\text{SO}_4$ , &c., and so to find the distribution of the interratomic actions in sulphates, nitrates, &c.

which the hands of a watch appear to move as we look at the face, the quartz is said to exhibit dextrorotatory power; this is expressed by prefixing + to the value of the angle of rotation. If the rotation takes place in the direction opposite to that in which the hands of a watch appear to move as we look at the face, the quartz is said to exhibit lævorotatory power; this is expressed by prefixing - to the value of the angle of rotation.

Optically active transparent media are those which rotate the plane of polarisation of a ray of light passed through them; they are divided into dextrorotatory substances, e.g. some specimens of quartz, sugar in aqueous solution, &c., and lævorotatory substances, e.g. other specimens of quartz, turpentine, quinine in alcoholic solution<sup>1</sup>, &c.

To determine the amount of rotation caused by any substance, it is necessary to have an instrument wherein a ray of light may be polarised, and the position of the plane determined; the polarised ray may be passed through a known quantity of the medium under examination; and finally the position of the plane of the emergent ray may be determined. Such instruments, known as *polarimeters* or *polaristrometers*, are described in detail in various text-books<sup>2</sup>.

Let us consider a liquid carbon compound, say  $C_{10}H_{16}$ . The angle of rotation,  $\alpha$ , depends on (1) the thickness of the layer of liquid through which the light passes, (2) the wave-length of the ray of light employed<sup>3</sup>, and in most cases, (3) the temperature at which the observation is made. The first of these conditions will be determined if we know the

<sup>1</sup> For details concerning polarised light, and circular polarisation considered from the physical stand-point, see Glazebrook's *Physical Optics*, chaps. XI. and XIV.

<sup>2</sup> See especially Armstrong and Groves, *Organic Chemistry*, 569 *et seq.*; and also Watts's *Dictionary*, 3rd Suppl. 1198—1207.

<sup>3</sup> The angle of rotation,  $\alpha$ , was supposed by Biot to vary inversely as the square of the wave-length of the light employed, but Boltzmann has shewn that the expression  $\alpha = \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$ , where  $B$  and  $C$  are constants determined experimentally, is a nearer approximation to the law: but the values of  $B$  and  $C$  appear to differ slightly for different media. See Watts's *Dict.* 3rd Suppl. 1207.

length of the column of liquid employed, and the second is rendered definite by making use of monochromatic light.

Let  $l$  = length of column of liquid in decimetres,  $d$  = density of liquid referred to water at  $4^{\circ}$ , and  $\alpha$  = angle of rotation of plane of polarisation of light of given wave-length; then

$$[\alpha] = \text{specific rotatory power of the liquid, for the given ray,} = \frac{\alpha}{l \cdot d}.$$

That is to say, the specific rotatory power of an optically active substance is the angle through which the plane of polarisation of a given ray is rotated by passing through a column 1 decimetre long of a liquid containing 1 gram of the substance in 1 cubic centimetre. If the substance to be examined is a solid, it must be dissolved in an optically inactive menstruum. In such a case, let  $l$  = length in decimetres of column of solution employed,  $p$  = grams of optically active substance in 100 grams of solution (i.e. gram-percentage composition), and  $d$  = density of solution referred to water at  $4^{\circ}$ ; then  $p \cdot d = c$  = concentration, i.e. grams of active substance in 100 c.c. of solution.

$$\text{Hence} \quad [\alpha] = \frac{100 \alpha}{l \cdot p \cdot d} = \frac{100 \alpha}{l \cdot c}.$$

As the value of  $[\alpha]$  generally rises as temperature rises<sup>1</sup>, thermometric observations must be made. The value of  $[\alpha]$  also varies with variations in (1) the nature, and (2) the quantity, of inactive solvent employed; the preceding formula therefore gives only the apparent specific rotatory power of the solid substance.

That  $[\alpha]$  varies according to the nature of the solvent, is shewn by Hesse's observations on turpentine oil<sup>2</sup>;

pure turpentine ( $C_{10}H_{16}$ )	oil + alcohol (amount of solvent varied in each case from 10 per cent. to 90 per cent.)	oil + benzene	oil + acetic acid
$[\alpha]_D$	37°01; 37°035 to 38°486; 37°194 to 39°449; 37°148 to 40°222.		

<sup>1</sup> For numbers illustrative of this in the case of aqueous solutions of tartaric acid see *Dict.*, 3rd Suppl. 1209.

<sup>2</sup> Hesse, *Annalen* 176. 89 and 189: see also Landolt's *Handbook of the Polariscopes* (English translation), 54—94. This book presents a very complete view of the whole subject of circular polarisation, chemically considered.

The following numbers<sup>1</sup> illustrate the dependence of  $[\alpha]$  on the amount of solvent employed ;

Aqueous solution of	Value of $[\alpha]_D$		Difference
	maximum	minimum	
Tartaric acid	+ 14°·18	+ 3°·20	10°·98
Codeine	- 137°·75	- 111°·50	26°·25
Quinine	- 169°·25	- 116°·0	53°·25

Landolt (*loc. cit.*) has shewn that the true value of  $[\alpha]$  may generally be found from a number of observations made with solutions of varying concentration ; the more concentrated the solution the more nearly does the value found for  $[\alpha]$  approach the true value, i.e. the more nearly does the observed, agree with the true specific rotatory power. It is better to use several solvents, and make a series of observations with each ; the value deduced for  $[\alpha]$  is generally the same for each solvent.

The nature and extent of the variations in  $[\alpha]$  caused by varying the quantity of solvent appear to differ for each optically active solid substance<sup>2</sup>; in some cases the relation is very complicated, in others it may be expressed by a comparatively simple formula<sup>3</sup>.

That the observed and calculated values of  $[\alpha]$  agree

<sup>1</sup> Landolt, *loc. cit.*

<sup>2</sup> The following numbers illustrate this statement (Landolt, *loc. cit.* 82):

Active substance.	Solvent.	$[\alpha]_D$ for pure substance.	$[\alpha]_D$ for maximum dilution.	Difference.
levorotatory turpentine	alcohol	36°·97	38°·79	+ 1°·82
dextrorotatory "	"	14°·17	15°·35	+ 1°·18
levorotatory nicotine .. .. .	alcohol	160°·83	138°·59	- 22°·24
	water	161°·29	74°·13	- 87°·16
dextrorotatory ethyl tartrate	alcohol	8°·27	10°·19	+ 1°·92
	water	8°·09	28°·12	+ 20°·03

<sup>3</sup> Thus, for solutions of turpentine in alcohol, Landolt gets the formula

$$[\alpha]_D = 36°·974 + \cdot 0048164g + \cdot 0001331g^2$$

where  $g$  = percentage of inactive solvent. (For more details see Landolt, *loc. cit.* 81—94.)

For a fuller treatment of the methods employed for finding the true value of  $[\alpha]$  from observations on solutions, see *Dict. 3rd Suppl.* 1212—1213.

closely, provided a sufficient number of observations is made, is evident from these results (Landolt).

Active substance	$[\alpha]_D$ observed	$[\alpha]_D$ calculated from observations on mixtures with					max. diff.
		(1) $C_2H_5OH$	(2) $CH_3OH$	(3) $H_2O$	(4) $C_2H_4$	(5) $CH_3CO_2H$	
Dextrorotatory ethyl tartrate }	8°·31	8°·27	8°·42	8°·09	—	—	-·22
Dextrorotatory turpentine }	14°·15	14°·87	—	—	—	—	+·72
Lævorotatory turpentine }	37°·01	36°·97	—	—	36°·97	36°·89	-·12
Lævorotatory nicotine }	161°·55	160°·83	—	161°·29	—	—	-·72

The true specific rotatory powers of camphor, cane sugar, and dextroglucose have been determined by Landolt, Tollens, and Schmitz<sup>1</sup>. But I think it should be noted that the observations on which the method for determining  $[\alpha]$  is based, were necessarily made with solutions of liquid compounds in inactive solvents, whereas in the cases of camphor and sugar we have to deal with solutions of solid substances; it is possible that the value of  $[\alpha]$  for liquid camphor may vary very much from that for solid camphor<sup>2</sup>. It should also be observed that any deductions concerning the relations between specific rotatory power and molecular structure, drawn from a study of liquid compounds, could not be applied in a precise manner to solid compounds, assuming the true value of  $[\alpha]$  for these compounds to be known.

145. In attempting to trace the relations which undoubtedly exist between the specific rotatory power and the structure of compounds, we must distinguish relationships between this constant and the composition of molecules whose empirical formulæ at least are known, from those between the same constant and such mixtures of molecules in varying proportions as are presented by solutions of known concentration.

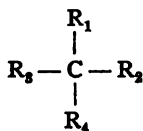
<sup>1</sup> See Landolt, *loc. cit.* 84—92; Tollens, and Schmitz in *Ber.* 9. 1531: 10. 1403; and *do.* 1414.

<sup>2</sup> Biot states that fused liquid tartaric acid is markedly dextrorotatory, but the solidified acid is feebly lævorotary (*Dict.* 3rd Suppl. 1209). Landolt's value of  $[\alpha]$  for solid camphor is 55°·6 (see *Dict.*, *loc. cit.* 374); while Gernez obtained the value 70°·33 for fused camphor (*do. do.* p. 1209).

For although in the latter cases no precise conclusions can be drawn regarding the relative arrangements of the atoms in the molecules, yet the study of specific rotatory power may help to throw light on such general questions as the action of solvents, the distinction between chemical and physical change, and so forth.

146. Most of the known compounds which possess the power of rotating the plane of polarisation of a ray of light contain carbon: van't Hoff, following in the steps of Le Bel, has endeavoured to trace a precise connection between the molecular structure of these compounds and their rotatory power. The molecule of every optically active compound, according to this hypothesis, contains one or more *asymmetric* atoms of carbon. The conception represented by this expression is essentially crystallographic.

An *asymmetric atom of carbon* directly acts on, and is acted on by, four, chemically different, monovalent atoms, or groups of atoms, within the molecule;—thus

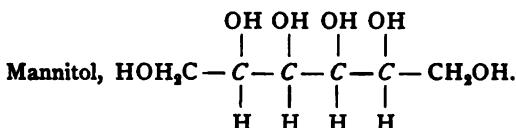
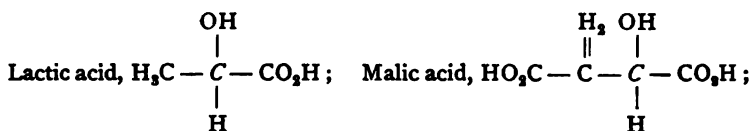


To render the conception more definite, the carbon atom is supposed to be situated at the centre of a tetrahedron and each monovalent radicle at one of the summits. Inasmuch as these radicles are chemically different, the action and reaction between each and the carbon atom is supposed to be different; hence each radicle is situated at a different distance from the central atom of carbon; and hence the tetrahedron is irregular, has no planes of symmetry, and is capable of existing in non-superposable (*enantiomorphous*) forms. Optical activity is regarded as always accompanied by such an arrangement as this of atoms in molecules, which molecules have thus the properties of partially developed non-superposable crystals<sup>1</sup>.

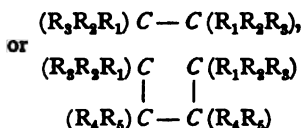
<sup>1</sup> For a more detailed account of van't Hoff's hypothesis, see *Dict. 3rd Suppl.* 1214—1217; or Armstrong and Groves, *loc. cit.* 986—993.



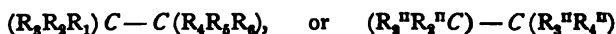
Representing the *asymmetric* carbon atom (or atoms) in a molecule by an *italicised C*, we have such formulæ as these ;



Any compound, the molecule of which contains a single asymmetric carbon atom, may exist in two optically different modifications. When more than one asymmetric atom is present, the number of possible modifications is conditioned by whether the formula of the compound is *symmetrical* or *unsymmetrical*: a *symmetrical formula*, in the nomenclature of this hypothesis, is one in which the radicles directly connected with the different asymmetric carbon atoms are the same; if these radicles, or some of them, are different, the formula is said to be *unsymmetrical*. Thus the formula



is symmetrical: but the formula

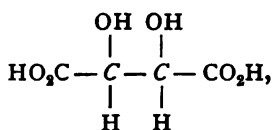


is unsymmetrical.

A carbon compound of unsymmetrical formula, containing  $n$  asymmetric atoms of carbon, may exist in  $(2)^n$  modifications; if the compound is represented by a symmetrical formula, it

may exist in  $(2)^{\frac{n}{2}} + \frac{(2)^n - (2)^{\frac{n}{2}}}{2}$  forms<sup>1</sup>. Thus tartaric acid is represented by the formula

<sup>1</sup> See illustrations of these equations in *Dict. 3rd Suppl.* 1138-39; or Armstrong and Groves, *loc. cit.* 987-990.



which is symmetrical, and contains two asymmetric atoms of carbon. The van't Hoff hypothesis asserts the possible existence of three optically different tartaric acids, which may be represented by the symbols

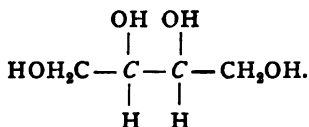
$$(1) +A + A (=2A), \quad (2) +A - A (=0), \quad (3) -A - A (=2[-A]);$$

where each part of the symmetrical molecule,



is represented by the sign  $A$ ; the symbol  $+$  or  $-$  being prefixed according as this group is regarded as being dextro- or lævorotatory. One of the hypothetically possible tartaric acids ought therefore to be dextro- and one lævorotatory; the third ought to be inactive, because of the balance of dextro- and lævorotatory powers within the molecule. Now three such acids exist<sup>1</sup>.

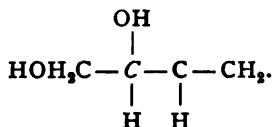
When a substance is regarded as being inactive because of the balance of opposite rotatory powers by the structure of the molecule itself, it is said to be inactive by *internal compensation*. But a substance may also be inactive by *external compensation*. Thus erythritol is probably represented by the symmetrical formula containing a pair of asymmetric carbon atoms



This substance is said to be optically inactive because of

<sup>1</sup> Racemic acid is probably a molecular compound of the dextro- and lævorotatory acids.

*internal compensation.* But by distillation with formic acid erythritol yields the glycol



This glycol, although containing one asymmetric carbon atom, is inactive. But the hypothesis asserts that two optically different modifications of this glycol may exist: if we suppose that both are actually produced, and produced in equal molecular quantities, we have an explanation of the non-activity of the glycol; it is inactive by *external compensation*.

This explanation appears to me to require that we regard the glycol in question as owing its optical inactivity to the existence of molecular groups, each composed of two chemically identical but optically dissimilar molecules: it could scarcely be that a *mixture* of the dextro- and lævorotatory molecules would always give an inactive substance which could not be separated into its optically different parts.

Many carbon compounds said to contain asymmetric carbon atoms are optically inactive. This does not seem to me to be a material objection to the van't Hoff hypothesis. Because when we speak of an asymmetric carbon atom, we mean more than is symbolised by the expression  $\text{CR}_1\text{R}_2\text{R}_3\text{R}_4$ ; we mean not only that the carbon atom is in direct union with four chemically unlike monovalent radicles, but also that the structure of this group,  $\text{CR}_1\text{R}_2\text{R}_3\text{R}_4$ , is of a special kind, and of a kind which, by the very terms of the hypothesis, cannot be distinguished from other possible structures by any chemical methods we at present possess. Whether a structure  $\text{CR}_1\text{R}_2\text{R}_3\text{R}_4$  shall or shall not be associated with optical activity, depends (by hypothesis) on the relative arrangement in space of the five parts which compose the structure; but this again depends on the equality or non-equality of the mutual actions between C and  $\text{R}_1$ , C and  $\text{R}_2$ , C and  $\text{R}_3$ , and C and  $\text{R}_4$ ; and this, finally, depends on the chemical nature of

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$ , using the expression *chemical nature* in its widest acceptance<sup>1</sup>.

We may object to the extremely crystallographic character of the van't Hoff hypothesis, and to the length to which it pushes the vague notion of 'bonds' or 'units of affinity', for it seems to regard these as capable of definite arrangement in space; but I think the hypothesis is worthy of careful consideration, because it draws attention to the inadequacy of the prevalent conceptions regarding isomerism and molecular structure, and because it bases the explanation it has to give of the connection between such structure and the properties of compounds on essentially dynamical conceptions.

But can it be shewn that optical activity is undoubtedly connected with the structure of the molecules of compounds, rather than with that of groups of molecules?

It is said<sup>2</sup> that the specific rotatory power of terpene ( $C_{10}H_{16}$ ) from French turpentine oil, and of camphor ( $C_{10}H_{16}O$ ), is independent of temperature, and is indeed the same for these substances in the gaseous as in the liquid state: if this is confirmed by further observations we shall have in these compounds instances of undoubted connection between molecular structure and rotatory power. But the great majority of optically active carbon compounds do not certainly exhibit such a connection, or exhibit it only in an indirect manner. Thus it cannot be asserted that the molecule of lactic acid ( $CH_3-CHOH-CO_2H$ ) is optically active, because no one has yet obtained molecules of this acid unmixed with molecules of other substances. Again, we do not know the true molecular weights of tartaric or malic acids: even in the cases of amylic alcohol, and valeric acid, which are gasifiable compounds, we cannot assert that the molecule  $C_4H_9 \cdot CH_2OH$ , or the molecule  $C_4H_9 \cdot CO_2H$ , is optically active, because the optical activity of the compounds in question belongs to them in

<sup>1</sup> For a tabular statement of compounds, shewing in what cases the presence of the structure symbolised by  $CR_1R_2R_3R_4$  is accompanied by optical activity, see Landolt, *loc. cit.* 27—9; see also table, *loc. cit.* p. 36. Just, *Annalen* 220, 146 has shewn that a number of derivatives of active amylic alcohol are themselves optically active.

<sup>2</sup> See *Dict. 3rd Suppl.* 1209.

the liquid, not in the gaseous, state. Moreover optically active amylic alcohol, or valeric acid, is easily changed by the action of heat into the inactive modification, and this change is said to be unaccompanied by any change in purely chemical reactions. Again, tartaric acid is supposed by the van't Hoff hypothesis to be active because of the structure of the molecule  $\text{CO}_2\text{H} - (\text{CHOH})_2 - \text{CO}_2\text{H}$ ; but the connection between the refrangibility of the light employed, and the observed values of  $[\alpha]$  for an aqueous solution of the dextrorotatory acid, of varying concentration, shews that this solution very probably contains a compound of the acid and water, of opposite optical power to that of the acid<sup>1</sup>. In other words mere solution in water has apparently sufficed to change the structure of the molecule of tartaric acid.

The great readiness with which the value of  $[\alpha]$  undergoes change when the compound exhibiting rotatory power is subjected to small physical changes, or is brought into contact with other compounds, appears to shew that in most cases at any rate, the power of rotating the polarised ray is to be regarded as a property rather of groups of molecules, than of the groups of atoms which form these molecules. But the power of forming groups characterised by such a marked property as optical activity, must be connected with the nature of the molecules which form these groups. We have seen that the nature of a molecule depends on the nature, number, and relative arrangement of its atoms: hence, in an indirect sense, optical activity is, on this view of the matter, to be associated with the structure of molecules.

147. Numbers have already been given shewing that the values of  $[\alpha]$ , determined for solutions of optically active compounds, vary in accordance with the nature and relative quantities of the solvents employed. A more detailed study of the connections between these constants serves to emphasise the dependence of rotatory power on the existence of groups of molecules.

Krecke<sup>2</sup> has attempted to generalise the relations between

<sup>1</sup> See *Dict. 3rd Suppl.* 1207—8.

<sup>2</sup> *Journal für prakt. Chemie* (2) 5. 6: see also Flavitsky, *Ber.* 15. 5.

the value of  $[\alpha]$  for a given compound, and for substances derived from it by the action of inactive solvents or chemical reagents: in these cases it is asserted that the so-called *molecular rotatory power*, i.e.  $([\alpha] \cdot M)$ , either remains unaltered, or is increased to a simple multiple of that of the original substance. But when we remember that the value of  $([\alpha] \cdot M)$  is known for very few compounds, we see that the means are wanting for proving or disproving the statement made by Krecke.

It seems at present impossible to foretell whether the optical activity of a compound will be altered or not, and if altered, in what direction the change will proceed, when the compound is mixed with optically inactive solvents. Thus, the rotatory power of an aqueous solution of tartaric acid is increased by addition of boric acid, but decreased by addition of hydrochloric or sulphuric acid. A solution of tartaric acid in absolute methylic alcohol is said to be inactive<sup>1</sup>, but a feebly lævorotatory solution of the same acid in acetone becomes dextrorotatory on addition of a little water.

Further, the simultaneous presence of two inactive solvents sometimes produces effects that would not be expected from the action of either separately. About one-half of the alcohol in an alcoholic solution of cinchonine may be replaced by chloroform without much alteration of rotatory power, but if as much as  $\frac{1}{800}$ th of the chloroform in a solution of the same alkaloid in this solvent is replaced by alcohol a marked change in rotatory power occurs<sup>2</sup>.

It seems probable that in at least the majority of cases where the rotatory power is considerably modified by addition of optically inactive bodies, this modification is to be connected with the formation of more or less unstable groups of molecules, and so with the production of a liquid in which groups of different degrees of complexity are simultaneously present<sup>3</sup>. Instructive illustrations of the modification in question are presented by milk sugar and by the glucoses

<sup>1</sup> Landolt, *Ber.* 6. 1078.

<sup>2</sup> *Dict.* 3rd Suppl. 1210.

<sup>3</sup> For details concerning modification of rotatory power by action of solvents or reagents, see Landolt, *loc. cit.* 35—41.

$C_6H_{12}O_6 \cdot H_2O$ . When a freshly prepared aqueous solution of one of these substances is kept at a given temperature for some time, the value of  $[a]$  gradually decreases until a certain limit is reached. The final value is more quickly attained by boiling the solution; on the other hand cold decreases the rate at which the value of  $[a]$  diminishes. Thus,

	Value of $[a]_D$	
	immediately after preparation of solution	after rotation has become constant
Dextrorotatory milk sugar	$80^{\circ}68$	$53^{\circ}63$
„ honey sugar	$91^{\circ}0$	$46^{\circ}58$

Now each of these sugars exists in a crystalline and in an amorphous form, the latter being produced from the former by fusion. As a solution in water of the amorphous form has a constant rotatory power, equal to the smallest value found for a solution of the corresponding crystalline form, it is concluded that the latter solution, when freshly prepared, contains groups of molecules of different complexity, of which some, and these the least stable groups, exhibit a much higher rotatory power than others<sup>1</sup>.

The facts known concerning optically active crystalline solids are on the whole in keeping with the view that the rotatory power of these substances is connected with the existence of more or less complex groups of molecules. All substances known to be optically active in the state of crystalline solids, with the exception of two<sup>2</sup>, lose their rotatory power when liquefied by fusion or when dissolved. These substances all crystallise in partially developed non-superposable forms. Inasmuch as they are inactive when the crystalline structure is destroyed, there must be an intimate connection between the power they possess of rotating a polarised ray, and the arrangement of the particles which compose their crystals.

Pasteur supposed that the smallest crystalline particle of one of these substances is composed of molecules arranged in right- and left-handed spirals, each spiral being non-super-

<sup>1</sup> Landolt, *loc. cit.* 62.

<sup>2</sup> These exceptions are *Strychnine sulphate* and *Amphetamine alum*.

possible on the other, and that when the crystals are liquefied by fusion, or are dissolved, this peculiar structure is destroyed, and with it the power of rotating a polarised ray is removed. This hypothesis has been so far confirmed by Sohncke, who has arranged thin plates of mica to represent Pasteur's spiral groups of molecules, and has thus obtained an optically active substance<sup>1</sup>.

148. Researches on the relations between the composition and the absorption-spectra of carbon compounds have been conducted by Hartley<sup>2</sup>. This chemist has shewn that the normal alcohols,  $C_nH_{2n+1}OH$ , do not absorb any of the ultra-violet rays; that the normal acids,  $C_nH_{2n+1}CO_2H$ , cause a slight absorption of these rays, the intensity of the absorption increasing as the molecular weight of the acid increases; and that benzene and its derivatives exhibit strong absorption, and are characterised by the appearance of absorption-bands, the position of which can be determined when a transparent diluent is added.

From an examination of the absorption-spectra of very many carbon compounds, Hartley concludes, that absorption-bands are never present in the ultra-violet part of the spectrum obtained by passing light through a compound in the molecule of which the carbon atoms are arranged in an 'open chain', but that such bands are present in the absorption-spectra of all benzene derivatives. Inasmuch, however, as benzene hexchloride  $C_6H_6Cl_6$  is very transparent, and exhibits no bands, it would appear that the mere closing of the chain of carbon atoms is not the sole condition necessary for the production of absorption-bands. Hartley thinks that each carbon atom must be in direct union with at least three other carbon atoms.

This supposition is in accordance with the observation, that solutions of naphthalene, anthracene, and phenanthrene, in transparent media, shew absorption-bands, similar to, but

<sup>1</sup> For details see Landolt, *loc. cit.* 19—20; or *Dict. 3rd Suppl.* 1214.

<sup>2</sup> *Phil. Trans.* 170. 257. See also *C. S. Journal Trans.* for 1881. 153 *et seq.* See also report of the B.A. committee on Spectrum Analysis; *Brit. Ass. Reports* for 1880. 258 *et seq.*



lower in refrangibility than, the benzene bands; and that these solutions likewise exhibit much more intense absorption than benzene.

Terpenes ( $C_{10}H_{16}$ ) and camphor ( $C_{10}H_{16}O$ ) exhibit more intense absorption than compounds of the paraffinoid group, but no bands appear in the spectra of the light transmitted by these compounds; hence their molecular structure appears to be related on the one hand to the paraffinoid and on the other to the benzenoid group of compounds.

By taking advantage of the differences in the character of the absorption exhibited by different compounds,—e.g. the character of the absorption-spectrum of cymene is very different from that of the terpenes,—it is possible to detect minute quantities of certain compounds in presence of large quantities of others, and also broadly to classify carbon compounds into groups. Further, by taking advantage of the differences in the positions of the bands in the spectra of the light transmitted by isomeric compounds, it will be possible, when sufficient data have been obtained, to determine the class to which this or that isomeride belongs. Moreover, the gathering together of this data will doubtless be the means of gaining much precise knowledge regarding the relations between the molecular structure and the actinic properties of compounds<sup>1</sup>. For the experiments of Hartley<sup>2</sup> tend to the conclusion that although greater or less absorption is connected with molecular vibrations, yet the special selective absorption characteristic of benzenoid compounds is rather to be connected with atomic vibrations. These experiments also shew that the mean rate of vibration of the rays absorbed by molecules of naphthalene and anthracene, is less than that of the rays absorbed by benzene molecules, and hence, remembering the similarity of the character of the absorptions in these three cases, it is concluded that the amplitudes of the vibrations of the naphthalene and anthra-

<sup>1</sup> For the application of his general conclusions to essential oils, quinoline, hydrocyanic and cyanuric acids, &c., see Hartley, *C. S. Journal Trans.* for 1880. 676; do. for 1882. 45; and *Chem. News*, 40. 269.

<sup>2</sup> *C. S. Journal Trans.* for 1881. 165—167.

cene molecules are greater, and the rates of vibration are slower, than those of the benzene molecules. Hence it would follow that the atomic vibrations which probably give rise to the observed selective absorption are closely dependent on the vibrations of the molecules as wholes.

Now if a connection between the vibrations of molecules and the vibrations of parts of these molecules is established, and if this connection is elucidated by precise data, we shall certainly have made an important advance in solving the fundamental problem of chemistry, which is to trace the relations between the composition and the properties of bodies.

A further step in this direction has been made by Abney and Festing<sup>1</sup>, who, by mapping the absorption which occurs in the infra-red region of the spectrum, have been able to shew that there is a definite connection between the nature of the atomic groups in the molecules of many carbon-compounds, and the vibrations of the rays stopped by these compounds.

149. The preceding paragraphs of this section will, I think, shew how promising of important results is the application of optical methods to the problems of chemical statics. That a relationship exists between refractive power and molecular structure, and also between rotatory power and molecular structure, has been established. In the hypothesis of Brühl, which connects the former physical constant at once with the valencies of atoms and with the distribution of atomic interactions, and in that of van't Hoff, which has a more kinetical aspect than the hypotheses regarding molecular composition at present dominant in chemistry, we have guides to future research. But much more data, dealing with groups of allied compounds, must be brought together before either of these hypotheses can be fully tested<sup>2</sup>.

<sup>1</sup> *Proc. R. S.* 31. 416, and *Phil. Trans.* for 1881, 7887.

<sup>2</sup> Reference may here be made to a paper by G. Krüss [*Ber.* 15. 1243, and 16. 2051] on an optical method for determining whether or not chemical action has occurred between two substances in solution, all the possible products of the reaction being also soluble under the experimental conditions. The method consists, essentially, in comparing the sums of the absorption-spectra of the original liquids with the absorption-spectrum of a mixture of these liquids.

SECTION III. *Methods based on determinations of the constant,*  

$$\frac{\text{formula-weight}}{\text{specific-gravity}}.$$

150. The quotient obtained by dividing the formula-weight by the specific gravity of a compound (referred to water at 4°) is generally called the *specific volume* of that compound. The term *specific volume*, however, evidently expresses the relative volume of unit weight of the substance. The quotient in question is sometimes called the *molecular volume* of the compound formulated. This expression strictly interpreted implies that the formula-weight is identical with the molecular weight, and that the specific gravity and formula-weight are expressed in terms of the same standard.

The value of  $\frac{\text{formula-weight}}{\text{spec. gravity}}$  is equal to the product of specific volume multiplied into molecular weight, assuming the latter to be the same as the formula-weight; or we may say that, if the weight expressed by the formula is taken in grams, the quotient  $\frac{\text{formula-weight}}{\text{spec. gravity}}$  represents the number of cubic centimetres occupied by an amount of the substance in grams proportional to its molecular weight. Now we can determine the molecular weights of gaseous compounds only: if the specific gravities of these compounds are referred to hydrogen as unity, then,  $\frac{\text{molecular weight}}{\text{spec. gravity}} = c$ , and  $c = 2$ . Never-

<sup>1</sup> It may be well to gather together here references to the most important articles and papers on the subject of this section:—KOPP, *Annalen* 98. 153, 303; 100. 19, &c. BUFF, *Annalen Supplbd.* 4. 129, and *Ber.* 4. 647. THORPE, *C. S. Journal Trans.* for 1880. 141, 327. L. MEYER, *Annalen Supplbd.* 5. 129; also *Die modernen Theorien* (4th Ed.), 284—292. ELSÄSSER, *Annalen* 218. 302. WEGER, *Annalen* 221. 61. WATTS'S *Dict.*; 1. 440 *et seq.* and (more especially) 3rd *Suppl.* 2117 *et seq.* RAMSAY, *C. S. Journal Trans.* for 1879. 463; *do.* for 1881. 49. 66. LOSSEN, *Annalen* 214. 81. Compare also SCHIFF, *Ber.* 14. 2761; 15. 1270; *Annalen* 220. 71, 278. SCHALFEJEW, *Ber.* 15. 2209; 16. 1853. See also O. E. MEYER'S *Die Kinetische Theorie der Gase*, 216—221. KRAFFT, *Ber.* 15. 1687. WILSON, *Proc. R. S.* 32. 457.

theless, if the quotient  $\frac{\text{formula-weight}}{\text{spec. gravity}}$  is obtained for a number of liquid compounds, we shall have a series of comparable values, which,—if formula-weight of liquid is a simple multiple of molecular weight of gas,—represent the volumes occupied by quantities of various liquid compounds proportional to the molecular weights of the same compounds in the state of gases.

The meaning to be attached to the expression 'volume occupied by a quantity proportional to molecular weight' will be discussed in paragraph 156.

The name *atomic volume* is generally applied to the quotient  $\frac{\text{atomic weight}}{\text{spec. gravity of liquid element}}$  (water = 1).

The determinations of the specific gravities of liquids necessary for finding values for the quotient we are discussing, should be made under comparable conditions as regards pressure. This condition is fairly fulfilled by determining the specific gravities at the boiling points of the liquids<sup>1</sup>.

151. Let the quotient  $\frac{\text{formula-weight of liquid compound}}{\text{spec. gravity referred to water at } 4^{\circ}}$  be expressed by the symbol (*V*). Then the value of (*V*) for a compound is said to be equal to the sum of the values of (*V*) for the elementary atoms which form the molecule of that compound. But has each elementary atom a constant value?

For many carbon compounds Kopp has shewn that

$$(\textit{V}) \text{C}_x\text{H}_y\text{O}_z = (x \cdot 11) + (y \cdot 5.5) + (z \cdot 7.8).$$

But in some cases the observed value of (*V*) does not agree with that calculated by this formula; thus

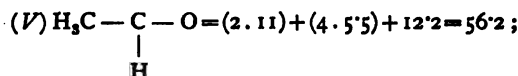
Aldehyde $\text{C}_2\text{H}_4\text{O}$ :	calculated ( <i>V</i> )	$= (2 \cdot 11) + (4 \cdot 5.5) + 7.8 = 51.8$ :	diff.
	observed ( <i>V</i> )	$= 56.5$	+ 4.7
Acetic acid $\text{C}_2\text{H}_4\text{O}_2$ :	calculated ( <i>V</i> )	$= (2 \cdot 11) + (4 \cdot 5.5) + (2 \cdot 7.8) = 59.6$ :	
	observed ( <i>V</i> )	$= 63.5$	+ 3.9

<sup>1</sup> Full details regarding the methods for accomplishing this will be found in Thorpe's paper, *loc. cit.*; see also Ramsay (*loc. cit.*) and Schiff (*loc. cit.*).

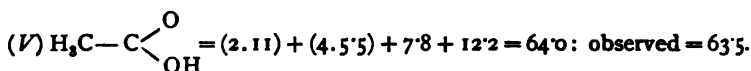
The value of ( $V$ ) for a compound  $C_xH_yO_z$  is conditioned, according to Kopp, by the value of ( $V$ ) for the oxygen atom, or atoms, in the molecule. Kopp gives the following two values, according as the oxygen atom acts as a monovalent or divalent atom in the given molecule<sup>1</sup>.

$$(V) O^I = 12.2; \quad (V) O^{II} = 7.8.$$

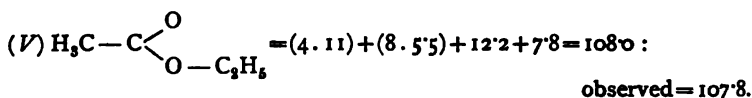
Applying these values to the case of aldehyde, we have



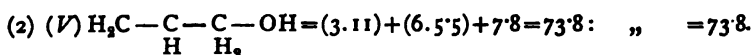
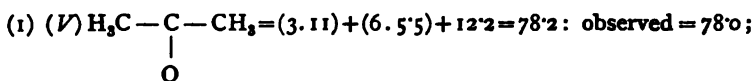
a result which agrees very closely with the observed value, viz. 56.5. For acetic acid we have



Or again, for ethylic acetate,



Or, once more, for acetone and its isomeride allylic alcohol,



Instead of assigning two values to the oxygen atoms in compounds of the form  $C_xH_yO_z$ , it would probably be better to employ the value, ( $V$ )  $CO = 23.2$  (i.e.  $11 + 12.2$ ), which attributes the influence on the total value of ( $V$ ) due to the presence of the group  $CO$  to both the atoms which comprise this group.

Schiff (*loc. cit.*) concludes that the value of ( $V$ )  $O^{II}$  varies according to the nature and arrangement of all the con-

<sup>1</sup> Kopp used the expression 'oxygen within the radicle' as synonymous with what is now called divalent (singly-linked) oxygen atoms; and 'oxygen without the radicle' as synonymous with monovalent (doubly-linked) oxygen atoms.

stituents of the molecule; and also, that the value of  $(V)X-C-O$  is always greater than that of  $(V)C-O-X$ , when  $X$  represents a radicle.

Kopp deduced two values for  $(V)S$ ; thus  $(V)S^I = 28.6$ ,  $(V)S^{II} = 22.6^1$ : but only one value for  $(V)C$ , and one for  $(V)H$ , and  $(V)Cl$ . Many, and very varying values, have been found by different observers for  $(V)N$ : thus Kopp assigns the value 2.3 to  $(V)N$  when  $N$  occurs in amines, and 17 when  $N$  occurs in  $CN$  and in some nitro-compounds; Ramsay gives  $(V)N = 3.6$  in amines, = 9.0 in pyridine, lutidine, &c., and = 7 in aniline, toluidine and dimethylaniline.

152. If the influence exerted by the oxygen in a carbon compound on the value of  $(V)$  for that compound, varies, according to the actual valencies of the oxygen atoms in the molecule, it appears probable that the total value of  $(V)$  will also depend on the actual valencies of the carbon atoms in the molecule. Buff<sup>2</sup> thought that his determinations shewed that the value of  $(V)$  for compounds containing tri-valent (doubly-linked) carbon atoms is greater than the value calculated on the assumption that  $(V)C^{III} = (V)C^{IV} = 12.2$ . Thus,

- (1) Dichlorethylene  $Cl_2 = C^{III} - C^{III} = H_2$ ,  $(V) = 79.9$ :  
 $(V)$  calculated = 78.6; diff. = 1.3+.
- (2) Carbon tetrachloride  $Cl_4 = C^{III} - C^{III} = Cl_4$ ,  $(V) = 115.4$ :  
 $(V)$  calculated = 113.2; diff. = 2.2+.
- (3) Amylene  $\begin{matrix} H_3C^{IV} \\ H_3C^{IV} \end{matrix} > C^{III} - C^{II} - C^{III}H_3$ ,  $(V) = 112$ :  
 $(V)$  calculated = 110; diff. = 2.0+.
- (4) Valerylene  $H_3C^{IV} \begin{matrix} \nearrow C^{III} \\ H \end{matrix} - C^{II} - \begin{matrix} \nwarrow C^{III} \\ H \end{matrix} - C^{IV}H_3$ ,  $(V) = 104.0$ :  
 $(V)$  calculated = 99; diff. = 5.0+.
- (5) Diallyl  $H_3C^{III} - \begin{matrix} C^{III} \\ H \end{matrix} - \begin{matrix} C^{IV} \\ H_2 \end{matrix} - \begin{matrix} C^{IV} \\ H_2 \end{matrix} - \begin{matrix} C^{III} \\ H \end{matrix} - C^{III}H_3$ ,  $(V) = 126.8$ :  
 $(V)$  calculated = 121; diff. = 5.8+.

No trustworthy conclusions regarding the values to be assigned to  $(V)C^{III}$  or  $(V)C^{IV}$  can however be drawn from

<sup>1</sup> See also Ramsay, *C. S. Journal Trans.* for 1879. 471-2.

<sup>2</sup> *Annalen, Supplbd.* 4. 143 et seq.

these data, because when we tabulate the values of ( $V$ ) for a number of hydrocarbons we find no apparent regular connection between these values and the valencies of the carbon atoms. Thus,

(1) Hexane  $\text{H}_3\text{C}-(\text{CH}_2)_4-\text{CH}_3$  ( $V$ )=140: ( $V$ ) calculated=143.

(2) Diallyl  $\text{H}_2\text{C}-\underset{\text{H}}{\text{C}}-\underset{\text{H}_2}{\text{C}}-\underset{\text{H}_2}{\text{C}}-\underset{\text{H}}{\text{C}}-\text{CH}_2$  ( $V$ )=126.8: „ „ =121.

(3) Benzene  $\begin{array}{c} \text{CH} \\ \text{HC} \diagup \text{CH} \\ | \quad | \\ \text{HC} \diagdown \text{CH} \\ \text{CH} \end{array}$  ( $V$ )=96: „ „ =99.

If we associate the increase in the value of ( $V$ ) for diallyl over the calculated value, with the presence of trivalent carbon atoms, then we must conclude, that in the molecule  $\text{C}_6\text{H}_6$ , the presence of trivalent carbon atoms is connected with a decrease in the calculated value of ( $V$ ), or that all the carbon atoms in this molecule are tetravalent.

153. But not only may the values to be assigned to carbon and oxygen atoms, in determining the total value of ( $V$ ) for a carbon compound, vary according to the actual valencies of these atoms in the molecule of the compound in question, but also, apparently, in accordance with the distribution of the interatomic reactions in molecules wherein all the carbon atoms are tetravalent, and all the oxygen atoms divalent. Thorpe (*loc. cit.*) has given some examples of such variations; but Zander<sup>1</sup> has extended the number of examples considerably. Thus a comparison of ( $V$ ) for propyl and isopropyl compounds shews that the normal compounds always exhibit a smaller value than the iso-compounds:

	$\text{C}_2\text{H}_5\text{OH}$	$\text{C}_2\text{H}_5\text{I}$	$\text{C}_2\text{H}_5\text{Br}$	$\text{C}_2\text{H}_5\text{Cl}$
highest value of ( $V$ ) obtained for normal compound $\left( \text{H}_3\text{C}-\underset{\text{H}_2}{\text{C}}-\underset{\text{H}_2}{\text{C}}-\text{X} \right)$	81.4	108.2	97.5	91.7
lowest value of ( $V$ ) obtained for iso-compound $\left( \text{X}-\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{CH}}} \right)$	82.3	108.3	99.0	93.0

<sup>1</sup> *Annalen* 214. 138: 224. 56.

but the molecules of both classes of compounds contain only tetravalent carbon atoms<sup>1</sup>.

Lossen<sup>2</sup> has collected the most trustworthy data bearing on the question as to whether or not a constant value can be assigned to  $(V)CH_3$ . Kopp gave 22 as the mean value for this group. Lossen shews that the differences between the values of  $(V)$  for successive homologues of the acid series  $C_nH_{2n+1}CO_2H$  nearly agree with the differences calculated on the basis of  $(V)CH_3 = 22$ ; but that in the series of alcohols  $C_nH_{2n+1}CH_2OH$  the value of  $(V)CH_3$  varies from 18·7 to 21, assuming that the other atoms exert a constant influence on the total value of  $(V)$ . Apparently then a variable value must be assigned to  $(V)C^{IV}$ , or to  $(V)H$ , or to both of these quantities.

Some light is thrown on this point by Zander's comparison (*loc. cit.*) of  $(V)$  for propyl, isopropyl, and allyl compounds, which leads to the conclusion that the difference between  $(V)$  for a normal propyl and the corresponding allyl compound, i.e. between two compounds differing in composition by  $H_2$ , varies from 5·7 to 8·9 (having a mean value of 7·1): hence, if we assume that the difference in question is wholly due to the difference in empirical composition, we appear forced to conclude that the value of the influence exerted on  $(V)$  by the monovalent atom H is variable<sup>3</sup>.

Thorpe (*loc. cit.*) got these results for compounds containing only tetravalent carbon atoms in their molecules:

<sup>1</sup> See also Brown, *Proc. R. S.* 26. 238. Also Elsässer, *Annalen* 218. 302.

<sup>2</sup> *Annalen* 214. 81 *et seq.*

<sup>3</sup> Besides the empirical difference of  $H_2$ , there is a difference in the actual valencies of some of the carbon atoms in propyl and allyl compounds; thus, normal propylic alcohol =  $H_3C - \underset{H_2}{C} - \underset{H_2}{C} - OH$ , and allylic alcohol

=  $H_2C^{III} - \underset{H}{C}^{III} - \underset{H_2}{C} - OH$ . See also Weger, *Annalen* 221. 61, who gets different

values for  $(V)CH_3$  in different series of compounds. See *Ber.* 16. 2458, where Kopp reminds us that this number was given by him as a *mean value*, and nothing more. Schiff (*Annalen* 220. 286, and 291) concludes that  $(V)C$  almost certainly varies according to the nature and the arrangement of the constituents of the molecule in which C occurs.



$\text{H}_2\text{CCl}_2 (V) = 65.12$ ; hence  $(V)\text{Cl} = 21.6$ ; (assuming  $(V)\text{C} = 11$ ,  
and  $(V)\text{H} = 5.5$ )

$\text{HCCl}_3 (V) = 84.53$ ; "  $(V)\text{Cl} = 22.7$

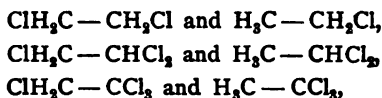
$\text{CCl}_4 (V) = 103.68$ ; "  $(V)\text{Cl} = 23.2$

Taking the mean value for  $(V)\text{Cl}$ , viz. 22.7, and applying this to calculate the values of  $(V)$  for each of the preceding compounds, we have

$(V)\text{H}_2\text{CCl}_2 = 67.4$	observed = 65.12	diff. = 2.28 -
$(V)\text{HCCl}_3 = 84.53$	" = 84.53	" = 0.0
$(V)\text{CCl}_4 = 101.8$	" = 103.68	" = 1.88 +

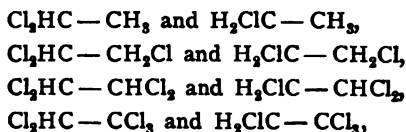
Hence the value of  $(V)\text{Cl}$  appears to be variable. This is more strikingly illustrated by Stædel's comparison<sup>1</sup> of the differences in the values of  $(V)$ , and also the differences in the boiling points, at various pressures, of chlorine compounds derived from  $\text{C}_3\text{H}_4$ .

The differences in  $(V)$ , and also in B.P. between the following pairs of compounds, viz.



express differences corresponding with change of  $\text{CH}_3$  into  $\text{CH}_2\text{Cl}$ , i.e. with the introduction of the first chlorine atom in place of an atom of hydrogen into the hydrocarbon residue  $\text{CH}_3$ .

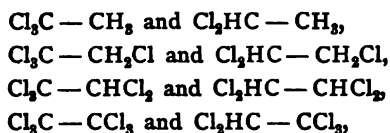
The differences in the values of the same quantities between the following pairs of compounds, viz.



express differences corresponding with the introduction of the second chlorine atom (in place of an atom of hydrogen) into the residue  $\text{CH}_3$ .

<sup>1</sup> Ber. 15. 2559.

And lastly, by comparing ( $V$ ) and B.P. for the following pairs of compounds, viz.:



the differences corresponding with the introduction of the third chlorine atom into the group  $\text{CH}_3$  are determined.

Now the differences in question are:

for the first chlorine atom	( $V$ ) = 14.20 :	B.P. = 56°.22 ;
„ second „	( $V$ ) = 16.37 :	B.P. = 31°.30 ;
„ third „	( $V$ ) = 19.16 :	B.P. = 16°.04.

Hence each chlorine atom has a different 'volume-value' and a different 'boiling-point-value.' If we choose to attribute the observed differences to the carbonaceous parts of the molecules, i.e. to  $\text{C}_3\text{H}_4$  in  $\text{C}_3\text{H}_4\text{Cl}_3$ , to  $\text{C}_2\text{H}_3$  in  $\text{C}_2\text{H}_3\text{Cl}_2$ , &c., we seem still obliged to admit that carbon *and* hydrogen atoms have varying 'volume-values', and varying 'boiling-point-values', in the molecules formulated.

154. The remark made in paragraph 151 that the value of ( $V$ ) for a compound is equal to the sum of the values of ( $V$ ) for each of the elementary atoms in the molecule of that compound, must evidently be supplemented by the statement, that in the case of carbon compounds, at any rate, the value of ( $V$ ) is not constant for C or O, and probably not for H or Cl, but varies in accordance with (1) the actual valencies of the former pair of atoms, and (2) the distribution of all the atomic interactions in the molecule. The precise character of the connection between the values of ( $V$ ) for C, O, H, and Cl, and the valencies on the one hand, and the nature of the atoms (or atomic groups) in direct union within any molecule on the other hand, cannot be ascertained until much more experimental data has been accumulated<sup>1</sup>. The known data regarding the values of ( $V$ ) cannot therefore be

<sup>1</sup> It is pointed out by Lossen (*loc. cit.*) that careful determination of ( $V$ ) for many series of carbon compounds and for many individuals in each series, are now required.

applied in other than a very tentative way to the selection of one from among several possible structural formulæ<sup>1</sup>.

155. The values of  $(V)$  for many solid compounds have been compared, and attempts have been made to generalise the relations between these values; but, as might be expected from considering how little comparable are the conditions under which the densities of solids have been determined, the conclusions are either vague and difficult of precise application, or represent only interesting relations between certain numbers, without much, if any, connection with chemical facts.

By considering the difference between  $(V)MO$  and  $(V)M$ , a fairly constant value for  $(V)O$  in the oxides is sometimes obtained: thus for  $PbO$  and  $Fe_3O_4$ , the difference in question is about 5.5. But in other oxides the value of  $(V)O$  appears to be very variable; thus,

$$(V)CuO - (V)Cu = 5.1; \text{ but } (V)Cu_2O - (V)Cu = 10.5.$$

Brauner and Watts<sup>2</sup> have drawn the following conclusions from comparisons of  $(V)MO$  and  $(V)M$  for different series of oxides.

(1) In strongly basic oxides the value of  $(V)O$  is negative; the more basic the oxide, and the greater the value of  $(V)M$  in the oxide, the more negative is the value of  $(V)O$ .

(2) In oxides of heavy metals and non-metals the value of  $(V)O$  is positive.

(3) In oxides of the earth metals the value of  $(V)O$  is *nil*.

The values of  $(V)$  for isomorphous compounds generally vary little; thus,

$$\begin{array}{ll} (V)MgO \cdot Al_2O_3 = 41.4 & (V)ZnO \cdot Fe_2O_3 = 47.0 \\ (V)ZnO \cdot Al_2O_3 = 40.2 & (V)MnO \cdot Cr_2O_3 = 46.4. \end{array}$$

The greater the agreement between the angles of crystals

<sup>1</sup> An illustration of the difficulties which are met with, and of the uncertain nature of the results obtained, is furnished by the contradictory conclusions of Thorpe (see Watts's *Dict.* 3rd Suppl. 2117—18) and of Masson and Ramsay (see *C. S. Journal Trans.* for 1881, 51 *et seq.*) regarding the structural formula of  $POCl_3$ . Thorpe concludes that the formula ought to be written  $Cl_2 = P - O - Cl$ , Masson and Ramsay think that  $Cl_3 \equiv P - O$  more nearly represents the facts.

<sup>2</sup> *Phil. Mag.* [5] 11. 60.

belonging to the same class, the less does the value of ( $V$ ) differ, e.g.

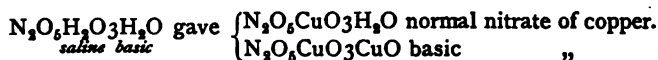
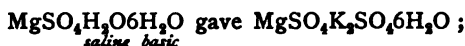
( $V$ )  $\text{SrCO}_3 = 41.0$  } crystals are almost identical.  
 ( $V$ )  $\text{PbCO}_3 = 41.2$  }

( $V$ )  $\text{BaCO}_3 = 45.8$  crystals exhibit differences from those of  $\text{SrCO}_3$  and  $\text{PbCO}_3$ .<sup>1</sup>

Kopp<sup>2</sup> has concluded that if  $D$ , the difference between what he calls the 'molecular volumes' of two isomorphous compounds, is represented as  $D = \frac{(V) - (V_1)}{\frac{1}{2}[(V) + (V_1)]}$ , then the value of  $D$  may attain a maximum, equal to 0.328, without isomorphism being impossible.

Determinations of ( $V$ ) for anhydrous and hydrated salts promise to throw some light on various questions implied in the commonly used expressions 'water of crystallisation' and 'water of constitution.'

Graham distinguished 'saline' water from 'basic' water in salts and acids; the replacement of the former by another salt, or by an oxide, produced a double—or in the case of acids a normal—salt; the replacement of the 'basic' water in an acid produced a basic salt. Thus,



Graham further distinguished *basic* water from *water of constitution*; e.g.



Thorpe and Watts<sup>3</sup> have determined ( $V$ ) for the salts  $\text{MSO}_4$ , when  $M = \text{Mg, Zn, Cu, Mn, Fe, Co}$ ; and for the hydrated salts  $\text{MSO}_4 \cdot x\text{H}_2\text{O}$  when  $M = \text{Mg, Zn, \&c.}$  and  $x$  varies from 1 to 7.

<sup>1</sup> For more details see Naumann's *Handbuch der Allgemeinen und Physikalischen Chemie*, 360—362.

<sup>2</sup> *Annalen* 36. 1. *Pogg. Ann.* 52. 262; 53. 446; 56. 371. See also article "Isomorphie," in the *Neues Handwörterbuch der Chemie*.

<sup>3</sup> *C. S. Journal Trans.* for 1880, 102.

The value of  $(V)\text{MSO}_4$  was found to be independent of the nature of M for the dehydrated salts. The difference  $(V)\text{MSO}_4 \cdot x\text{H}_2\text{O} - (V)\text{MSO}_4$  gave the increase in  $(V)$  for  $x\text{H}_2\text{O}$  added to the salts. The following results were obtained.

Mean difference in value of

$(V)\text{S}$	and $(V)\text{S} \cdot \text{H}_2\text{O} = 10.7$
$(V)\text{S} \cdot \text{H}_2\text{O}$	„ $(V)\text{S} \cdot 2\text{H}_2\text{O} = 13.3$
$(V)\text{S} \cdot 2\text{H}_2\text{O}$	„ $(V)\text{S} \cdot 3\text{H}_2\text{O} = 14.5$
$(V)\text{S} \cdot 3\text{H}_2\text{O}$	„ $(V)\text{S} \cdot 4\text{H}_2\text{O} = 15.4$
$(V)\text{S} \cdot 6\text{H}_2\text{O}$	„ $(V)\text{S} \cdot 7\text{H}_2\text{O} = 16.2$

$$[(V)\text{S} = (V)\text{MSO}_4, (V)\text{S} \cdot x\text{H}_2\text{O} = (V)\text{MSO}_4 \cdot x\text{H}_2\text{O}.]$$

Hence the value of  $(V)\text{MSO}_4 \cdot x\text{H}_2\text{O}$  is influenced in a different degree by each of the molecules of water which combines with the salt; or, it may be said, that the water molecules contribute in unequal degrees towards the total value of  $(V)$ .

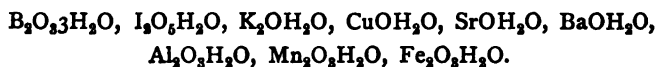
Clarke<sup>1</sup> has compared the differences between  $(V)$  for hydrated and  $(V)$  for dehydrated salts, belonging to two classes of compounds.

In the first class, where  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Mg}, \text{Cu}, \text{Fe}, \text{or Co}$ , and  $x$  varies from 2 to 6, the mean value of

$$\frac{(V)\text{MCl}_2 \cdot x\text{H}_2\text{O} - (V)\text{MCl}_2}{x}$$

was found to be  $= 13.76$  (with a maximum value of 15.0, and a minimum of 12.5).

The second class comprised various hydrated oxides and hydroxides, viz.



In this class the value of the difference

$$\frac{(V)\text{oxide} \cdot x\text{H}_2\text{O} - (V)\text{oxide}}{x}$$

varied from 7.4 to 19.4.

If S represent one of the chlorides belonging to the first class, or one of the oxides belonging to the second class, then, for class I, the formula  $(V)\text{S} \cdot x\text{H}_2\text{O} = (V)\text{S} + (x \cdot 13.76)$  gives

<sup>1</sup> *Amer. Journal of Sci. and Arts*, (3). 8. 428.

results which agree fairly well with the observed results ; but no such simple relation between  $(V)S \propto H_2O$  and  $(V)S$  can be traced among the results obtained for compounds belonging to class II.

But the hydrates of class I belong to the group of compounds containing 'water of crystallisation,' whereas those of class II, or most of them at any rate, belong to the group containing 'water of constitution'; hence, although the results obtained by Thorpe and Watts (*loc. cit.*) lead to the conclusion that the value of  $(V)H_2O$  in the salts  $MCl_x \cdot xH_2O$  is probably different for each addition of  $H_2O$ , nevertheless Clarke's numbers, taken as a whole, emphasise the difference between 'water of crystallisation' and 'water of constitution,' and shew that the chemical difference implied in these expressions is connected with the relative magnitudes of the spaces occupied by chemically comparable quantities of hydrated salts belonging to each group of compounds.

156. The quotient  $\frac{\text{formula-weight}}{\text{specific gravity}}$  has been treated as an empirically determined quantity: incidentally it has been regarded as expressing the volume occupied by a quantity of the compound formulated proportional to the weight of the molecules which form the vapour of that compound. The question is often propounded in papers on '*Specific volumes*', whether the volume of an element in the free state is, or is not, identical with the volume of the same element in combination. This question, it seems to me, may be better put in another form. What is the connection between the value of  $(V)$  for a given compound, and the nature and arrangement of the atoms which constitute the molecule of that compound? It has been shewn (pars. 152, 153) that the partial value to be assigned to each atom is not a constant quantity; in other words that  $(V)$  varies with variations in the arrangement, no less than in the nature of the atoms which form the molecule of the compound for which  $(V)$  has been determined. But is there any connection between the variations of  $(V)$ , the valencies of the atoms on the one hand, and the distribution of the interatomic reactions on the other? From the

data concerning isomeric carbon compounds, firstly, containing only saturated polyvalent atoms, and secondly, containing also unsaturated polyvalent atoms, we may conclude, I think, that both connections exist. It seems probable that a decrease in the actual valency of an atom, other things remaining the same, is attended by an increase in the value of ( $V$ ). But Stædel's investigation (par. 153) shews that the latter value is also modified by the nature of all the atoms in the molecule. If these connections can be made precise, and their nature ascertained by careful investigation, it may become possible to trace relations between the volumes occupied by molecules of defined structure and the energy-differences of these molecules, and perhaps to connect with these, the differences in the values of the refractive, and the rotatory powers, of the same molecules<sup>1</sup>.

If the value of ( $V$ ) for a compound is regarded from the point of view of the molecular theory, a connection may be traced between this value, and the partial value of ( $V$ ) for each atom in the molecule of the compound. For it has been shewn by L. Meyer<sup>2</sup>, and by Loschmidt<sup>3</sup>, that the spaces occupied by gaseous molecules (calculated from data based on the transpiration-coefficients of the substances) are connected with the atomic structure of these molecules, in the same general way as has been shewn by Kopp and others to hold in the case of liquid compounds<sup>4</sup>. The Clausian sphere-of-action (*wirkungssphäre*) of a molecule is the smallest space which the molecule can occupy under given conditions. Changes in these conditions (e.g. change of temperature), changes in the form of the molecule, or changes in the arrangement of the atoms in the molecule, will be accompanied by changes in the

<sup>1</sup> We should thus gain clearer conceptions of the properties of atoms as these are exhibited in atomic interactions, and also be able to connect, in a more precise manner than is yet possible, these interactions with the properties of the systems thereby formed. If this view is accepted it is evident that the results obtained by the various physical methods discussed in this, and the preceding section, must have kinetical as well as statical aspects (see book II. chaps. III. and IV.).

<sup>2</sup> *Annalen*, Supplbd. 5. 129.

<sup>3</sup> *Sitzberichte der K. Akad. zu Wien (math.-naturwiss. classe)*. 52. (2nd part) 395.

<sup>4</sup> See O. E. Meyer's *Die Kinetische Theorie der Gase*, 216—221.

space occupied by the molecule. The relations between the values of these smallest spaces (spheres-of-action) occupied by the molecules of two gases can be calculated, by means of a formula deduced from the general principles of the molecular theory, from observations of the transpiration-coefficients of the gases. Putting the experimentally determined value of ( $V$ ) as the value of the molecular sphere-of-action of one of the gases, the values of the molecular spheres-of-action of other gases can be found, and compared with those calculated from Kopp's, Meyer's, and Loschmidt's values for  $\frac{\text{atomic weight}}{\text{specific gravity}}$  of nitrogen, oxygen, hydrogen<sup>1</sup>, &c., and from the partial values assigned, by different chemists, to various atoms in determining the total value of ( $V$ ) for molecules containing these atoms. This is done by O. E. Meyer (*loc. cit.* pp. 219—221). The observed and calculated values of ( $V$ ) agree as closely as could be expected, considering that regard has been paid in the calculations solely to volume, whereas the molecular spheres-of-action must be conditioned by the form, the diameter, and the length of the molecular systems<sup>2</sup>. Hence there is a well-established probability in favour of the conclusion that the partial values assigned to each atom, in determining the total value of ( $V$ ) for a liquid compound, are proportional to the volumes occupied by these atoms in the gaseous state. But this is just the conclusion drawn from an empirical study of the values of ( $V$ ) determined for series of liquid compounds. Much work must however be done before precise connections

<sup>1</sup> For a description of the determination of this constant for oxygen and other gases from measurements of the transpiration-coefficients of these gases, see L. Meyer, *Annalen*, Supplbd. 5. 129.

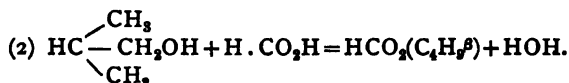
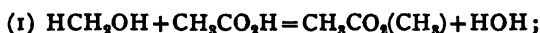
<sup>2</sup> Meyer (*loc. cit.* pp. 213—216) concludes that probably the atoms in the molecules  $H_2$ ,  $Cl_2$ ,  $O_2$ ,  $N_2$ ,  $HCl$ ,  $NO$ ,  $H_2O$ , and  $H_2S$  are arranged rectilinearly in an open chain; the atoms in the molecules  $CO_2$ ,  $N_2O$ ,  $C_2N_2$ , and  $NH_3$  are arranged in one plane but not rectilinearly; the atoms in the molecule  $CH_4$  form a sphere; and those in the molecules  $CH_3Cl$ ,  $C_2H_4$ ,  $C_2H_5Cl$ , and  $C_2H_6O$  form oblate spheroids. Boltzmann [*Wied. Ann.* 18. 309 (also *Ber.* 16. 772)] has drawn conclusions as to the forms of various molecules, from determinations (chiefly those made by Strecker) of the ratio of specific heat at constant pressure to that at constant volume.



can be traced between the total value of ( $V$ ) and the partial values assigned to the various atoms in any molecule.

SECTION IV. *Method based on the determination of 'Etherification-values'.*

157. The rate of formation of ethereal salts by the mutual actions of alcohols and carbon-containing acids has been studied by Menshutkin: many of his results have a direct bearing on the questions of chemical kinetics, some of them however may find a place here. The standard reactions in terms of which determinations are stated are these,



By varying the alcohol in (1) and the acid in (2), comparable series of values are obtained for (1) alcohol-acetic system, and (2) acid-isobutylic system. The number of molecules of  $\text{HCH}_2\text{OH}$  decomposed in reaction (1), and the number of molecules of  $\text{HCO}_2\text{H}$  decomposed in reaction (2), when equilibrium is established, are taken as 100, and the results with other alcohols and acetic acid, or with other acids and isobutylic alcohol, are stated in terms of this unit.

The expression 'etherification-velocity' is used to denote the amount of action during one hour; the expression 'etherification-limit' is used to denote the amount of action when equilibrium is established. Thus the statement 'the *etherification-velocity* of  $\text{CH}_3\text{CH}_2\text{OH}$  is 67.3, and the *etherification-limit* is 95.6' means, that when equal numbers of molecules of  $\text{CH}_3\text{CH}_2\text{OH}$  and  $\text{CH}_3\text{CO}_2\text{H}$  react, 67.3 molecules of  $\text{CH}_3\text{CH}_2\text{OH}$  are decomposed during the first hour, and 95.6

<sup>1</sup> The papers by Menshutkin, of which this section is a very condensed summary, will be found in *J. für prakt. Chemie*, (2) 24. 49; do. 25. 193, and 203 (abstracts in *C. S. Journal* for 1881. 1117; 1882. 384, 485, and 595). Abstracts will also be found in *Ber.* 14. 2630, 2819; 15. 162, 248, and 721. A paper containing a summary of Menshutkin's results will be found in *Ann. Chim. Phys.* (5). 30. 81. (Abstract in *C. S. Journal* for 1884. 726.)

when the action ceases, the number of molecules of  $\text{HCH}_2\text{OH}$  decomposed under similar conditions (at the close of the reaction) being taken as 100<sup>1</sup>.

158. The following, among many other numbers, were obtained by Menshutkin.

*Alcohol-acetic system.*

Formula of alcohol.	Velocity.	Limit.
$\text{HCH}_2\text{OH}$	80.0	100.0
$\text{CH}_3 \cdot \text{CH}_2\text{OH}$	67.3	95.6
$\text{C}_2\text{H}_5 \cdot \text{CH}_2\text{OH}$	66.9	96.0

Hence, the substitution of  $\text{CH}_3$  for H in the primary alcohol  $\text{H} \cdot \text{CH}_2\text{OH}$  appears to be accompanied by a decrease in the *etherification-velocity* of about 12.5, and in the *limit* of about 4.5.

The following conclusions are drawn by Menshutkin from his determinations of the reaction-values of the system  $\text{R} \cdot \text{CH}_2\text{OH} + \text{CH}_3\text{CO}_2\text{H}$ .

(1) The reaction-values (i.e. velocity and limit) of the normal group  $\text{C}_n\text{H}_{2n+1}$  in the alcohols  $\text{C}_n\text{H}_{2n+1}\text{CH}_2\text{OH}$  are practically the same.

(2) Isomerism in the  $\text{C}_n\text{H}_{2n+1}$  radicles of primary alcohols influences only the velocity-value, not the limiting value.

(3) Unsaturated alcohols ( $\text{R} \cdot \text{CH}_2\text{OH}$ ) exhibit lower reaction-values than saturated alcohols; e.g. the values for  $\text{C}_2\text{H}_5 - \text{CH}_2\text{OH}$  are smaller than those for  $\text{C}_2\text{H}_5 - \text{CH}_2\text{OH}$ .

From his study of the etherification of secondary alcohols,  $\text{R}_2\text{CHOH}$ , the same chemist concludes that these alcohols exhibit lower values than primary alcohols; and that the same radicle has smaller values in a secondary than in a primary alcohol. The limiting value for tertiary alcohols cannot be determined on account of the occurrence of secondary changes; the velocities shew great irregularities.

Further results obtained by Menshutkin shew that definite connections, the nature of which cannot yet be precisely

<sup>1</sup> The process is conducted at 153°—154°; the residual acid is determined by titration. Two to five grams of alcohol are sufficient, and the process is always applicable except the ethereal salt produced happen to be unstable at the temperature of experiment.

traced, exist between the actual valencies of the atoms, and also the distributions of the interatomic reactions in the molecules of alcohols, and the etherification-values of these alcohols<sup>1</sup>.

By multiplying the limiting value of each compound by the molecular weight of that compound (and dividing by 100), numbers are obtained which exhibit the influence, on the etherification-limit, of the molecular weights of the members of the system studied. Menshutkin gives the following numbers as representing *molecular limits*. In a later paper he calls these numbers simply *weight-limits*, in distinction to the *percentage limits* already explained.

*Acid-isobutylic system.*

Acid.	Molecular limit.	Difference for each CH <sub>2</sub> .
CH <sub>3</sub> CO <sub>2</sub> H	40.42	10.41
C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	50.83	
(C <sub>3</sub> H <sub>7</sub> <sup>a</sup> )CO <sub>2</sub> H	61.17	10.34
(C <sub>4</sub> H <sub>9</sub> <sup>a</sup> )CO <sub>2</sub> H	80.98	$9.90 = \frac{19.81}{2}$
(C <sub>7</sub> H <sub>15</sub> <sup>a</sup> )CO <sub>2</sub> H	102.05	$10.53 = \frac{21.07}{2}$

Mean difference for each increment of CH<sub>2</sub> = 10.29.

The value of the molecular, or weight, limit for any member of this series of acids (the alcohol being isobutylic) may be found by the formula,

$$\text{molecular limit} = 40.42 + (n - 2) 10.29;$$

when  $n$  = number of carbon atoms in the molecule of the acid.

Thus, in the acid (C<sub>3</sub>H<sub>7</sub><sup>a</sup>) CO<sub>2</sub>H  $n = 4$ , hence

$$\text{molecular limit} = 40.42 + (2 \cdot 10.29) = 61.0; \text{ observed value} = 61.17.$$

Menschutkin gives the expression  $a + (n - 2)d$  for finding the molecular etherification-limit for an acid in any system of alcohol and acids, when  $a$  = molecular limit for the first acid of the series, and  $d$  = mean increase, for each increment of CH<sub>2</sub>, in the molecular limit of the acids of the series.

<sup>1</sup> For a more precise statement of Menshutkin's conclusions on this point see abstract in *Ber.* 14. 2818.

The rule is, to the value of the limit for the given alcohol with the first acid of the series, add  $(n-2)d$ , that is, add  $(n-2)$  times the mean homologous difference (i.e. the mean difference for each increment of  $\text{CH}_2$ ) between the weight-limits of the given acid and the first acid of the series, when  $n$  = number of carbon atoms in the molecule of the given acid.

Thus, required the weight-limit for the caproic-butylic system. For the acetic-butylic system  $a = 40.52$ , and  $d = 10.29$ ; caproic acid is  $\text{C}_6\text{H}_{12} \cdot \text{CO}_2\text{H}$ ; therefore the weight-limit required is  $40.52 + (4 \cdot 10.29) = 81.68$ .

It is evident that the percentage limit can easily be found when the values of  $a$  and  $d$  are given. In the case in question we have,

$$\text{percentage limit} = \frac{81.68 \cdot 100}{116} = 70.41. \quad [\text{C}_6\text{H}_{12} \cdot \text{CO}_2\text{H} = 116].$$

Menschutkin gives the following values for  $a$ , and  $d$ , in various systems of alcohols, and acids of the acetic series :

acid-ethylic	system ; $a = 39.94$	} $d = 10.29.$
acid-propylic	„ ; $a = 40.23$	
acid-butylic	„ ; $a = 40.42$	
acid-amylic	„ ; $a = 40.55$	
acid-hexylic	„ ; $a = 40.64$	
acid-heptylic	„ ; $a = 40.71$	
acid-caproic	„ ; $a = 40.77$	

It is also possible to vary the alcohol, the acid remaining constant, and from data obtained to calculate the weight-limit for any given system<sup>1</sup>.

From a comparison of the etherification-values for primary, secondary and tertiary acids, and also of the same values for hydroxy- and chloro-acids, &c., Menschutkin draws certain conclusions regarding the connections between the variations in these values and the molecular structures of the various acids. For instance, the velocity of etherification of the primary acids is much greater than that of the secondary acids, but the limiting values are nearly identical in both series.

<sup>1</sup> See details in *C. S. Journal, Abstracts for 1882, 387.*

A study of these conclusions shews that much is to be hoped for from the application of Menshutkin's method, but that more data must be obtained before we have precise knowledge concerning the connections in question<sup>1</sup>.

*Concluding Remarks on Part I.*

159. The general aim of the first part of this book has been to give a fairly complete account of the present state of knowledge regarding the questions of chemical statics, indicating where such knowledge requires to be chiefly supplemented, or rendered more precise, by new experimental researches.

I have regarded those questions which are concerned with substances, or systems of substances, in equilibrium as broadly belonging to chemical statics; but I have been obliged to pay more or less attention to the kinetical aspects presented by all such questions.

It may be said that the fundamental conception of atom and molecule, stated and illustrated in chapter I., has been regarded in its applications to explain resemblances and differences between physical and chemical phenomena, nascent actions, allotropy, isomerism, and the classification of elements and compounds; and that the principal methods, both purely chemical and chemico-physical, which are employed in examining these problems, have been sketched, and their applications illustrated.

A way has thus been cleared by which we may hope to approach the more difficult problems of chemical kinetics.

<sup>1</sup> See some of Menshutkin's generalisations in *C. S. Journal*, *Abstracts* for 1882, 485, 598: and an application to the formulæ of maleic and fumaric acids in *do. do.* 1882, 383.

Schiff (*Annalen* 223. 47; abstract in *C. S. Journal* for 1884, 808) has determined the 'coefficients of capillarity' of a number of liquid carbon compounds. There appears to be a distinct connection between the values of this constant and the nature, number, and arrangement of the atoms in the molecules of the compounds examined.

Perkin has just published an extensive research into the connections between the composition of various carbon compounds and their power of rotating the plane of polarisation of a ray of light when under magnetic influence. (*C. S. Journal*, *Trans.* for 1884, 421 *et seq.*)

## BOOK II.

### CHEMICAL KINETICS.

#### CHAPTER I.

##### DISSOCIATION.

160. WE must now proceed to consider some of the phenomena which are connoted by the term chemical kinetics. In the introduction to book I. I said that this term is to be used as including the facts and principles which on the whole relate to chemical action, as opposed to those which are for the most part connected with chemical composition. We have however seen how impossible it is to carry out this division in any but the broadest way. We have seen that the same facts may be, indeed must be viewed, now from the statical, now from the kinetical stand-point. But while this is true, it is, I think, established by the history of chemistry that progress has been made at some periods more by seeking knowledge of the composition than of the reactions of compounds, while at other times inquiries into the functions rather than the composition of different kinds of matter have been most productive.

A chemical change must be looked at from two points of view; the relations between the reacting bodies, and the relations between the forces concerned in the change, must be studied.

161. The reactions of elements and compounds when produced in contact with other substances furnish problems for

the solution of which both statical and kinetical methods are required. Such reactions have been considered<sup>1</sup> from the point of view of the composition of the changing system, and some of them have been also regarded from the stand-point of thermal chemistry<sup>2</sup>. Emphasis was laid on the necessity of considering not only the composition of the whole changing system, but also the conditions under which the change proceeds, *e.g.* the relative masses of the reacting substances, the rate of evolution of the 'nascent' products, the temperature, &c.

162. The fifth section of the second chapter of book I. is occupied with questions which cannot be even approximately answered except by the help of essentially kinetical conceptions. We there learned to recognise the existence of substances intermediate between true compounds,—the properties of which are for the most part conditioned by the nature, number, and mutual interactions of the atoms which compose their molecules,—and true mixtures,—the properties of which are the means of those of their constituents. But the consideration of 'molecular compounds' led us to regard the chemical system of which such compounds form a part as continually undergoing change, and as held in equilibrium, as a whole, only by the mutual actions and reactions of its parts. In that section (par. 101) facts were stated which seemed to shew that molecules of different degrees of complexity may be simultaneously present in a gas. We found, for instance, (par. 101) that the gas obtained by heating phosphorus pentachloride contains molecules of  $\text{PCl}_5$  and  $\text{Cl}_2$  in addition to molecules of  $\text{PCl}_3$ ; and that as temperature rises the former kinds of molecules increase in number, while the latter decrease, until at a little above  $300^\circ$  no  $\text{PCl}_5$  molecules remain. The most simple and probable explanation of the numbers representing the vapour density of acetic acid at different temperatures and pressures is, that at temperatures below  $120^\circ$  (pressure being normal) the gas consists for the most part of molecules having the composition  $\text{C}_2\text{H}_4\text{O}_2$ , but that at  $250^\circ$  or

<sup>1</sup> Book I. chap. II. Section 1.

<sup>2</sup> Book I. chap. IV. pars. 122—124.

so (pressure being unchanged) the formula  $C_2H_4O_2$  represents the composition of by far the greater number of molecules which compose the gas. The explanation which was given of these and similar facts regarding the relations of the densities of gases to temperature and pressure was based on the kinetic theory of gases (see par. 101, pp. 207—8). If that explanation is accepted, it follows, I think, that the condition of a gas in which dissociation is proceeding must be such that the equilibrium momentarily established between molecules of different atomic composition is being continually disturbed, and fresh conditions of equilibrium are being established, which in turn last only for a very short time<sup>1</sup>.

In this gradual change of one kind of molecules into another kind brought about by the action of heat we have one of the distinctive features of dissociation, or thermolysis, the phenomena of which it is the object of the present chapter to examine<sup>2</sup>.

163. The term dissociation is generally used to indicate the resolution of more into less complex molecules, by the action of heat; the amount of resolution increasing as the temperature increases, and decreasing when the temperature decreases. For each substance there is a temperature at which the whole, or almost the whole, is converted into two or more new

<sup>1</sup> It has been asserted (Dewille and Troost, *Compt. rend.* 64. 237: 91. 54; Berthelot, *do.* 91. 77) that the observed changes in the densities of various gases, e.g.  $N_2O_4$ ,  $I_2$ , &c., at different temperatures are to be regarded as indicative of variations in the coefficients of expansion of these gases. If this is so, then the relations between the volumes of those gases and the temperature are very curious. The values of the coefficients of expansion of those gases which are generally supposed to dissociate when heated, must, on this view, be regarded as increasing rapidly with increase of temperature until a maximum is attained, and then again decreasing to a constant value. In connection with this subject it ought to be remembered that Gay-Lussac's coefficient of expansion (0.00365) is only approximate, that indeed Boyle's law is only approximately true, but that at the same time the relation between the volume and the temperature has been carefully examined for several gases, and it has been shewn that even at very high temperatures the coefficients of expansion of these gases are constant. [The gases in question are H, O, N, S, Te, Hg,  $CO_2$ , HCl,  $As_4O_6$ ; see V. Meyer, *Ber.* 13. 2021.]

<sup>2</sup> In connection with this subject generally see article 'Dissociation' in *Neues Handwörterbuch der Chemie*.



bodies<sup>1</sup>. If the temperature is now allowed to fall, the products of the original change gradually recombine until the initial state of the system is again attained. When on the other hand, a substance undergoes decomposition by the action of heat there is a certain temperature-interval within which the change, if started, goes to completion; moreover the initial state is not regained by allowing the products of the change to cool in contact with each other.

When a substance dissociates at least one of the products must be gaseous under the conditions of the experiment.

164. The process of dissociation presents some analogies with that of evaporation. In both there is a gradual change brought about by the action of heat. As the rate of evaporation is conditioned by the pressure exerted on the liquid by the vapour, so the rate of dissociation is conditioned by the sum of the partial pressures of the gaseous products of the action<sup>2</sup>.

For any temperature there is a certain pressure, such that when this is reached the process stops, but it may be again started either by decreasing the pressure or by increasing the temperature. This pressure has been called the dissociation-pressure, or better the equilibrium-pressure. Dissociation may therefore be stopped by allowing one or more of the gaseous products to accumulate in contact with the dissociating body; on the other hand dissociation may be caused to proceed rapidly by removing one or more of the gaseous products as quickly as it is produced.

Thus Wurtz found that the gas obtained by vapourising phosphorus pentachloride into an atmosphere of phosphorus trichloride was composed for the most part of molecules of  $\text{PCl}_5$ ; although when the same compound was vapourised at the same temperature into air the molecules of  $\text{PCl}_5$  were for

<sup>1</sup> The numbers given in par. 101 for the densities of various compounds sufficiently represent the gradual progress of dissociation-phenomena. A formula is given on p. 204 (note) by means of which the amount of dissociation of gaseous compounds may be calculated from observations of the densities at different temperatures.

<sup>2</sup> See especially Deville, *Compt. rend.* 56. 195; and *Leçons sur la dissociation*.

the most part dissociated into  $\text{PCl}_5$  and  $\text{Cl}_2$ .<sup>1</sup> So also Pebal<sup>2</sup> shewed that ammonium chloride may be permanently decomposed by vapourising it in an arrangement which permits of the rapid removal of the less dense product of dissociation, although when the same compound is vapourised into an enclosed space, and the products (ammonia and hydrochloric acid) are allowed to cool in contact with each other, the whole of the original substance is regained in the solid form.

165. When solid calcium carbonate is heated in a closed space lime and carbonic anhydride are formed, but on cooling calcium carbonate is reproduced.

Debray<sup>3</sup> has shewn that, at a red heat, the direction of this change is dependent only on the pressure. For each temperature there is a maximum pressure exerted by the gaseous carbon dioxide at which the direct change,  $x\text{CaCO}_3 = \text{CaO} + \text{CO}_2 + (x-1)\text{CaCO}_3$ , stops; at  $860^\circ$  this equilibrium-pressure = 81 m.m. of mercury and at  $1000^\circ$  it is equal to 520 m.m. If a system consisting of  $\text{CaO}$ ,  $\text{CaCO}_3$ , and  $\text{CO}_2$  is slowly cooled, the whole of the carbon dioxide is absorbed by the lime, but if the temperature is rapidly lowered some of the dioxide remains uncombined with the lime. If the temperature is slowly lowered a certain amount of carbon dioxide is absorbed, the pressure is changed, and the equilibrium is overthrown. But a new condition of equilibrium is attained, to be again destroyed by absorption of more carbon dioxide following on a further lowering of temperature. Finally stable equilibrium is attained when the whole of the dioxide has combined with the lime. If however the temperature is caused to decrease rapidly, the normal absorption of the dioxide corresponding to each change of temperature cannot be completed, and the cooled system is composed of chalk, lime, and carbon dioxide<sup>4</sup>.

166. Dissociation is thus essentially a reversible process<sup>5</sup>; it is accompanied by absorption of a definite quantity

<sup>1</sup> *Compt. rend.* 76. 601.

<sup>2</sup> *Annalen* 123. 199.

<sup>3</sup> *Compt. rend.* 84. 603.

<sup>4</sup> *Pogg. Ann.* 149. 222.

<sup>5</sup> "A physical process is said to be reversible, when the material system can

of heat which is again lost by the system as it passes back to its original configuration. We may picture to ourselves the action of heat as bringing about a separation of the molecules of the dissociating body into atoms, followed by a rearrangement of these atoms to form new molecules, the new system thus produced being dependent for its continued existence on supplies of energy from without itself; but when the supply of energy in the form of heat is stopped, we may suppose that the interatomic attractions bring back the system to its original molecular arrangement. When however a chemical decomposition occurs by the application of heat, the new configuration assumed by the atoms is stable, it does not require to be supplied with energy from without in order that it may continue to exist; hence there is no swinging back to the original state.

167. In the dissociation of calcium carbonate the system at any moment is composed of three distinct substances; a decrease in the amount of calcium carbonate is necessarily accompanied by an increase of lime and carbonic anhydride, and *vice versa*. If we study the processes of dissociation wherein more than one arrangement of the members of the system is possible, we shall find that the configuration assumed at any given temperature depends, as in the simpler case of calcium carbonate, solely on the pressure exerted by the gaseous products of the change.

Take, for instance, the two compounds,  $\text{AgCl} \cdot 3\text{NH}_3$  and  $2\text{AgCl} \cdot 3\text{NH}_3$ , produced by the action of ammonia on solid silver chloride. If silver chloride is brought into an atmosphere of ammonia, at ordinary temperatures, the ammonia is absorbed with formation of  $2\text{AgCl} \cdot 3\text{NH}_3$ , and the pressure falls; by increasing the quantity of ammonia absorption again proceeds, and so on. For every temperature there is a certain pressure whereat neither absorption or evolution of ammonia occurs; this equilibrium-pressure is independent of the relative

be made to return from the final state to the original state, under conditions which, at any stage of the reverse process, differ only infinitesimally from the conditions at the corresponding stage of the direct process." Clerk Maxwell; Article 'Diffusion' in *Encycl. Brit.* (9th ed.).

amounts of  $\text{AgCl}$  and  $2\text{AgCl} \cdot 3\text{NH}_3$  present<sup>1</sup>. When the equilibrium-pressure is reached, if the pressure of the ammonia in the apparatus is largely increased, absorption occurs and the compound  $\text{AgCl} \cdot 3\text{NH}_3$  is produced. For this compound also there is a pressure, corresponding to each degree of temperature, whereat equilibrium is established. The following table gives some of the equilibrium-pressures as determined by Horstmann<sup>2</sup>.

Temp.	Pressure in millimetres.				
	$\text{AgCl} \cdot 3\text{NH}_3$		$2\text{AgCl} \cdot 3\text{NH}_3$		
6°	...	...	...	...	22
7	...	...	...	...	23·4
8	...	...	432	...	24·9
9	...	...	446	...	26·5
10	...	...	465	...	28·2
12	...	...	520	...	31·9
16	...	...	653	...	40·9
18	...	...	723	...	46·6
20	...	...	793	...	52·6

The difference between the pressures corresponding to each of these compounds at any temperature is so great that it is comparatively easy to study the relations between pressure, temperature, and amount of chemical change for each compound: but when attempts are made to do this for hydrated salts, e.g.  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , it becomes almost impossible to determine the equilibrium-pressures for various temperatures. When hydrated copper sulphate is heated to a given temperature in an enclosed space the pressure of the water-gas evolved shews great fluctuations. At first sight it might be thought that the dissociation of this salt does not follow the ordinary rule, viz. that the equilibrium-pressure is independent of the relative amounts of decomposed and undecomposed solid substances present, and is dependent solely on the temperature. But on closer examination it is found that the solid undergoing dissociation is really a mixture of various hydrated salts, each with its own equilibrium-pressure, but that the differences between these pressures are small. In

<sup>1</sup> Horstmann, *Ber.* 9. 749; Isambert, *Compt. rend.* 66. 1259: 70. 456.

<sup>2</sup> *loc. cit.*

this case we have therefore a number of processes of dissociation proceeding simultaneously; hence we cannot expect to find a definite equilibrium-pressure for each temperature<sup>1</sup>.

The differences between the equilibrium-pressures of the various hydrates are so marked in the cases of some hydrated salts, that the phenomenon of dissociation can be shewn to follow the same course as with calcium carbonate, or the ammoniacal silver chlorides<sup>2</sup>.

168. In any dissociating system at the equilibrium-pressure, the number of molecular decompositions and recompositions must be regarded as equal in number during any given interval of time. A general theory of chemical change, including gaseous dissociation, based on the molecular kinetic theory of gases, has been developed by Pfaundler. This theory will be considered when we come to deal in detail with the subject of chemical change<sup>3</sup>. It is however difficult to reconcile Pfaundler's theory with the fact that the amount of dissociation of a solid, into solid and gaseous products, is independent of the relative quantities of the original substance and the solid product of dissociation. In the dissociation of calcium carbonate, e.g. we should expect, that the greater the amount of lime present, relatively to the amount of carbonate, the greater would be the chances that some of the CO<sub>2</sub> molecules should be caught and held fast, and that therefore the amount of dissociation at any temperature would depend upon the ratio between the lime and calcium carbonate actually present in the system at that temperature<sup>4</sup>. Pfaundler has very ingeniously tried to get over this difficulty<sup>5</sup> by referring the dissociation only to the molecules on the surfaces of the various members of the system. In gases all molecules may be regarded as being on the surface; but

<sup>1</sup> (See Naumann, *Ber.* 7. 1573.) It should be noted that the equilibrium-pressure for a given temperature is never attained immediately that temperature is reached; a little time must elapse before the entire system has settled down into equilibrium. See Horstmann, *Ber.* 9. 752, and Naumann, *Annalen* 160. 27.

<sup>2</sup> For numbers see Debray, *Compt. rend.* 66. 194.

<sup>3</sup> See *post*, chap. II. par. 187.

<sup>4</sup> See this difficulty stated by Horstmann, *Ber.* 9. 757.

<sup>5</sup> *Ber.* 9. 1152.

when a solid is present, only those molecules of the solid which can be directly bombarded by the gaseous molecules, are, in Pfaundler's language, on the surface. The number of surface-molecules is very small compared to the total number, hence a change in the relative amounts of the solid compounds present (call these AB and B) will be accompanied by a change in the ratio of surface-molecules of AB to those of B, small in comparison with the number of molecules of the gaseous body present (call this A); hence only a small change of pressure will occur, and this will quickly be rectified by the absorption (or evolution) of a little more of A. But all molecules of A must gradually come to the surface of AB, and take part in the exchange which is going on between AB and A; but the molecules of A which pass into the interior of the solids AB and B will remain there a comparatively long time, and hence will exert but a small influence on the pressure of the gas A.

Horstmann<sup>1</sup> has rather endeavoured to develop a general theory of dissociation from thermodynamical principles; he has deduced a formula from the second law of thermodynamics applicable to cases of dissociation, and generally to chemical changes brought about by the action of heat, and he has sought to shew that when the positive and negative changes are equal in a process of dissociation, i.e. when the equilibrium-pressure is reached, the entropy of the system has attained its maximum value. But the application of thermodynamical methods to questions of chemical equilibrium, including dissociation, will be considered in another chapter.

169. The special characteristics of dissociation which, taken together, mark it off from decomposition, are then briefly these<sup>2</sup>: (1) heat is absorbed, and the temperature of the dissociating system increases throughout the entire process; (2) the original configuration of the system is returned to, if the products of dissociation are allowed to cool in contact with each other; (3) the change is gradual, and

<sup>1</sup> *Annalen* 170. 192; see also *do. Supplbd.* 8. 112.

<sup>2</sup> See *Neues Handwörterbuch der Chemie*, 2. 999.

therefore at any given temperature the dissociation is partial, although the whole mass of the dissociating substance is submitted to the same thermal conditions as regards supply of heat from without; (4) the amount of dissociation is dependent on the temperature and pressure of the gaseous product or products; and (5) is independent of the ratio between the quantities of the solid products of the change present at any temperature<sup>1</sup>.

170. It is evident that the possible occurrence of dissociation must have an important bearing on determinations of the densities of gaseous compounds from which the molecular weights of these compounds are deduced<sup>2</sup>.

We have already learned (par. 101) that the density of the vapour of acetic acid decreases, as temperature increases, from the boiling point to about 100° above this point, after which it becomes constant. If the temperature is kept constant and the pressure is increased, the density of the vapour increases. The rate of change in the value of the density of this vapour, which accompanies change of temperature and pressure, is much more rapid than the rate of change in the value of the density of air under similar conditions; there are however no abrupt changes in the value under discussion. The smallest molecular formula assignable to acetic acid,

<sup>1</sup> It is probable that relatively less energy is transformed into heat in the formation of a dissociable compound from its constituents, than in the formation of an analogous compound which decomposes, but does not dissociate, when heated. If this is so, then perhaps the relatively small evolution of heat which attends the formation of the former compound may be connected with the existence of atomic groups in the molecule (or in the reacting unit) of this compound. When the compound is heated, it separates, on this supposition, into those groups the parts of which hold together; whereas when the other compound is heated much energy is absorbed, and the result is a separation of the molecules into their constituent atoms, which at once pair off into new molecules, so that the conditions required for the re-formation of the original compound no longer exist. This view may, I think, be shewn to be in keeping with Pfandl's theory of chemical equilibrium (see *post*, chap. II. par. 187). The ratio of the energy of rotation of the parts of the molecules to the energy of agitation of the molecules as wholes, would, on this view, be partly dependent on whether these molecules were built up of individual atoms, or of groups of atoms each of which was more thermally stable than the molecules themselves.

<sup>2</sup> See *ante*, book I. chap. I. par. 16.

which shall express its percentage composition [ $C=12$ ,  $O=16$ ,  $H=1$ ], is  $H_2CO$ ; the other possible formulæ are  $H_4C_3O_3$ ,  $H_6C_2O_2$ ,  $H_8C_4O_4$  &c., &c. Now if we tabulate the observed densities of acetic acid vapour at different temperatures, and compare them with the densities of the hypothetical compounds  $H_2CO$  &c. we have this result.

*Density of vapour of acetic acid at 760 mm.*

Temp.	Observed.	Calculated for formula.
125°	3'20	$C_4H_8O_4=4'15$
130	3'12	$C_3H_6O_3=3'11$
140	2'90	$C_2H_4O_2=2'08$
150	2'75	$CH_2O=1'04$
160	2'48	
170	2'42	
190	2'30	
200	2'22	
220	2'17	
230	2'09	
250	2'08	
300	2'08	

The progress of the change represented by the varying value of the density is very gradual; we cannot therefore suppose that each temperature on the table is marked by the presence of molecules of a definite weight, and by the presence of these molecules only. The process represented by these numbers is analogous to the processes of dissociation which we have considered; the explanation in terms of the kinetic theory of gases has already been given (par. 101, pp. 207—8), and has, I think, been shewn to be fairly satisfactory<sup>1</sup>. If that explanation is accepted it follows that the density of any chemically homogeneous vapour obtained by heating a liquid substance should not attain a constant value until the gas has been raised some degrees above the boiling point of the liquid. The temperature-interval through which the gas must be raised will vary, according to the nature of the gas, and of the liquid from which it is obtained. This theoretical deduction has been verified by experiments so far as these

<sup>1</sup> See in connection with this subject O. E. Meyer's *Die Kinetische Theorie der Gase*, pp. 76—82.



have yet extended<sup>1</sup>. Numbers have been given (par. 101, p. 209) which shew that constant values are obtained for the densities of the easily gasifiable elements chlorine and bromine, only at 150° or 200° above the boiling points of these bodies.

The numbers representing the density of the gas obtained by heating phosphorus pentachloride which are given in par. 101 (p. 204) shew, that even at about 30° above the boiling point of this compound the observed density is approximately 30 per cent. less than that calculated from the formula  $\text{PCl}_5$ . Wurtz<sup>2</sup> diffused the vapour of this compound, at temperatures a little below its boiling point, into a flask containing air; by determining the weight of the mixed gases (air and vapour of phosphorus pentachloride) and the volume of each, it was possible to calculate the partial pressure to which the latter was subjected. Some of Wurtz's results are given in tabular form; the volumes are stated in cc. and are reduced to 0° and 760 mm.

Temperature of experiment.	Volume of vapour of pentachloride.	Volume of air.	Density of vapour of pentachloride.	Partial pressure.
145°	85.1	123.0	6.70	311 mm.
137	39.75	165.15	6.47	148 "
129	52.8	179.0	6.63	170 "

The density of the gas obtained by vapourising phosphorus pentachloride under these conditions is only about 8 per cent. less than that required by the formula  $\text{PCl}_5$ .

Wurtz then diffused the vapour of the pentachloride into a flask containing a known amount of phosphorus trichloride vapour; from the sum of the weights of the two gases, and from analyses of the contents of the flask, he was able to calculate the volume and weight of the vapour from the pentachloride, and the pressure to which that vapour was subjected in the flask. As the mean of 12 experiments, at temperatures ranging from 160° to 175°, and pressures varying from 168 to 413 mm., Wurtz obtained the number 7.23 as representing the density of the vapour of phosphorus penta-

<sup>1</sup> See, for illustrations, Naumann's *Thermochemie*, pp. 155—8.

<sup>2</sup> *Compt. rend.* 76. 601.

chloride, obtained by gasifying this substance into an atmosphere of phosphorus trichloride.

Hence there seems to be little doubt that the so-called anomalous vapour density of phosphorus pentachloride is indicative of the dissociation of molecules of  $\text{PCl}_5$  into molecules of  $\text{PCl}_3$  and  $\text{Cl}_2$ .

There has been a great deal of discussion within recent years as to the action of heat on chloral hydrate. Does the vapour obtained by heating this substance contain chloral and water, or is it composed of chloral hydrate? The following results were obtained by Naumann<sup>1</sup>.

Temp.	Pressure.	Density		
		Observed	Calculated for	
			$\text{CCl}_3 \cdot \text{COH} + \text{H}_2\text{O}$	$\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$
100°	450·5 mm.	2·81		
78·5	162 „	2·83	2·86	5·72

Hence chloral hydrate appears to undergo complete dissociation into chloral and water at 78°, and under so small a pressure as 162 mm.

These numbers were not accepted by Troost, Berthelot, and others, as conclusive, because these chemists are opposed to the conceptions of modern chemistry which are founded on the distinction between atoms and molecules. As this distinction is an outcome of the application of Avogadro's law to chemical processes, it is evident that, could this law be overthrown, the distinction in question would appear to be less well grounded. Now if it could be proved that the density of a homogeneous gas is only half as great as the number calculated by the use of Avogadro's law, an important step would be made towards overthrowing the law in question.

It has been shewn that the vapour obtained by heating chloral hydrate diffuses as a mixture of chloral vapour and water and not as a homogeneous gas<sup>2</sup>; further that chloral vapour is not hydrated in the vapour obtained by heating chloral hydrate, provided the pressure of the former is greater

<sup>1</sup> *Ber.* 9. 822.

<sup>2</sup> Wiedemann and Schulze, *Wied. Ann.* 6. 293.

than the equilibrium-pressure of the latter at the temperature of experiment<sup>1</sup>; and also that the vapour in question behaves towards a hydrated or dehydrated salt in the same way as a gaseous mixture containing water<sup>2</sup>. Moreover Engel and Moitessier<sup>3</sup> have shewn that when chloral hydrate is distilled with chloroform at 60°, the distillate contains both water and chloral. Naumann has also proved that when chloral hydrate is distilled alone, the distillate contains much chloral and a little water, and the residue much water and a little chloral<sup>4</sup>. Finally the densities of the gases obtained by heating chloral-alcoholate<sup>5</sup> and butylchloralhydrate<sup>6</sup> shew that these compounds, which are analogous to chloral hydrate both in composition and function, undergo dissociation when heated. Hence there can be no doubt that the compound  $\text{CCl}_3\cdot\text{CH}(\text{OH})_2$  is dissociated, even at low temperatures and small pressures, into  $\text{CCl}_3\cdot\text{COH} + \text{H}_2\text{O}$ <sup>7</sup>.

171. The characteristic features of dissociation, as contrasted with decomposition, have already been summarised (par. 169). It is not possible however to define the term dissociation. There are many changes which present more or less close resemblances to well-marked processes of dissociation. Sometimes the resemblance is so close that we have little hesitation in classing the actions under the heading of dissociation; sometimes it is impossible to place the phenomenon entirely in the class of dissociation or in that of decomposition. Thus when hydrogen and water-vapour are passed over a mixture of iron and magnetic oxide of iron, it is found that a state of equilibrium is maintained for any given temperature, and that this equilibrium is independent of the relative quantities of the two solids present, and is conditioned only by the pressures of the water-vapour and

<sup>1</sup> Naumann, *Thermochemie*, 136.

<sup>2</sup> Wurtz, *Compt. rend.* 84. 977: 86. 1170: 90. 118, 337, 572.

<sup>3</sup> *Compt. rend.* 88. 285: 90. 97.

<sup>4</sup> *Ber.* 12. 738.

<sup>5</sup> Wurtz, *Compt. rend.* 85. 49.

<sup>6</sup> Engel and Moitessier, *Compt. rend.* 90. 1075.

<sup>7</sup> For a fuller discussion of the dissociation of chloralhydrate, see Naumann's *Thermochemie*, 134—137.

hydrogen, which pressures are always in the same ratio to each other as long as the temperature remains unchanged<sup>1</sup>.

Although there is here a more complex series of changes than in the cases of dissociation hitherto studied, yet because the change is brought about by raising the temperature, because the amount and direction of the change are dependent only on the temperature and the pressure of the gaseous components of the changing system, and because the change is reversible, we are entitled to class the reaction in question as a dissociation-phenomenon.

172. It has been experimentally proved that many salts—e.g. ammonium salts, many of the alums, cobalt chloride, sodium sulphate, &c.—are partially resolved into their constituents when dissolved in much water. Further, it has been shewn that the amount of this decomposition is dependent on the temperature and the relative masses of water and salt; and finally that the change can be, at least partially, reversed by lowering the temperature of the solutions<sup>2</sup>.

The action of the water in these changes has been compared to the action of the pressure of the gases produced in a process of dissociation. Dilution may thus be regarded as analogous to decreased pressure. But the analogy is misleading. In many if not all cases of so-called dissociation in solution, water is itself one of the components of the original substance; hence, judging from the analogy of gaseous dissociation, we should expect that as this product of the change accumulates the process would become slower and would eventually stop. But we find that increasing the quantity of water acts in the same way as decreasing gaseous pressure. The water probably exerts two actions; one, which may be called physical, whereby an increase in the quantity of water gives greater freedom of motion to the particles of the dissolved substance, and also lessens the chances of combination between the separated components of this substance; and

<sup>1</sup> Deville, *Compt. rend.* 70. 1105 : 71. 30.

<sup>2</sup> Examples will be found in Watts's *Dict. Suppl.* 2. 291 *et seq.* See also for the case of iron sulphate, chloride and nitrate, G. Wiedemann, *Pogg. Ann.* 126. 1 : 135. 177.

one, which may be called chemical, whereby any increase in the quantity of water brings about the formation or decomposition of definite compounds which would not otherwise be produced. While an increase in the quantity of water may, in one respect, tend to increase the amount of chemical change, it may, in the other respect, exert an opposite influence. When the first of these actions of water is much more marked than the second we shall have phenomena occurring which closely resemble those presented in gaseous dissociation<sup>1</sup>.

The influence exerted by varying the relative mass of the water present in such a process as the separation of ferric chloride into hydrochloric acid and soluble ferric hydroxide, suggests that certain classes of compounds, more especially such as contain water as one of their constituents, may be able to exist in the presence of water, although when the water is removed they separate into their constituent parts. This subject cannot however be considered until we have gained more knowledge of the conditions which affect the equilibrium of chemical systems<sup>2</sup>.

<sup>1</sup> For the fuller illustration and discussion of 'dissociation in solution,' see Naumann's *Thermochemie*, 158—167; and article 'Dissociation' in *Neues Handwörterbuch der Chemie*, especially pp. 999—1002.

<sup>2</sup> See *post*, par. 183.

## CHAPTER II.

### CHEMICAL CHANGE.

#### SECTION I. *General Considerations.*

173. PROCESSES of dissociation present examples of chemical systems maintained in equilibrium by the opposing actions of various forces. We have repeatedly had occasion to employ this conception in a general way in preceding chapters ; it remains now that we endeavour to make it somewhat more definite.

Many of the older chemists were accustomed to regard chemical change as a continuous process ; among those who made this conception prominent Berthollet and Davy are especially to be mentioned.

The early years of the present century are most important in the history of chemistry : in 1808 appeared Dalton's *New System* ; in 1803 Berthollet published his *Essai de Statique Chimique*.

Berthollet sought to explain chemical action as the result of attractions between the small particles of which bodies are composed<sup>1</sup>. These attractions are, he said, probably of the same kind as those between large masses of bodies ; in the latter cases we speak of the attraction of gravity, in the former of the attraction of affinity. This attraction between the small particles of bodies, when conditions are favourable, results first in cohesion, and then in combination. But other forces may come into play the results of which are opposed to those of the attraction of affinity ; heat may cause the

<sup>1</sup> See *post*, chap. III. par. 200.

expansion of substances which would otherwise combine; solution may weaken, or destroy, the cohesion of the particles of a solid. Whether combination occur or not, and if it occur, whether the products remain unchanged or not, depends, on Berthollet's view, upon the relative magnitudes of the opposing forces. If the attraction between the particles of different kinds of matter is greater than the action of the forces which tend to separate these particles, then a new compound, or compounds, will be formed. Should these compounds be solids under the experimental conditions, the cohesion of their particles will act in the same direction as the attraction of affinity which is the immediate agent in their production. The final arrangement of the particles of two kinds of matter depends, according to Berthollet, not only on the relative magnitudes of the different attractions between them, but also on the relative masses of the reacting bodies; thus a relatively small attraction may be made to overcome a greater, by largely increasing the mass of one of the two kinds of matter.

Berthollet regarded a liquid holding a solid in solution as a system in a state of more or less unstable equilibrium; by removing some of the liquid by evaporation, or by lowering the temperature, or in other ways, this equilibrium might be overthrown, and crystals would separate, containing particles both of the solid previously in solution, and also of water changed from the liquid to the solid state. Such a system, said Berthollet, will present two extreme cases, (1) all the solid is held in solution by the liquid, (2) all the liquid is changed to the state of solid. Between these extremes there may be many states each marked by a certain relation between the amounts of solid and liquid compounds; for Berthollet regarded the solution, no less than the crystals which separated, as a compound, or a series of compounds, of water and salt.

Combination and solution were looked on by Berthollet as analogous actions. 'In solution,' he said, 'one pays attention chiefly to the liquidity acquired by the solid by combining [with the solvent], and especially to the uni-

'formity of the parts of the liquid compound....In a combination one principally considers the other properties of the compound which is produced, comparing therewith the properties of the substances which produced it. In most cases solution is due to a combination so feeble that the properties of the dissolved substance do not disappear<sup>1</sup>.'

Again 'chemical action is reciprocal; its effect is the result of a mutual tendency to combination. One ought not, strictly speaking, to say that a liquid acts upon a solid, rather than that the solid acts upon the liquid; it is more convenient however to ascribe the whole of the action to one of the substances, when one wishes to examine the products of the action, rather than the action itself<sup>2</sup>.'

When lime is placed in water, mutual action, said Berthollet, begins at once, but the cohesion of the particles of the solid is so great that the dissolving action of the water does not produce any marked effect for some time; but water is being absorbed by the lime, and thus the effect of the cohesion of the particles of the lime is slowly overcome by that of the solvent action of the water, until finally the lime dissolves. During this process two combinations of lime and water are formed, one solid, the other liquid; the effect of one force, cohesion, is to increase the amount of the former; the effect of another force, solution, is to increase the amount of the latter combination. A state of equilibrium is established, and continues so long as the conditions are unchanged; but alteration of temperature, or changes in the relative masses of water and lime, suffice to overthrow this equilibrium and to establish another<sup>3</sup>.

Berthollet not only formed a clear mental image of a system as held in equilibrium by the actions and reactions of its various constituents, but he also had what I think must be regarded as a very clear conception of the chief forces concerned in maintaining this equilibrium. In the summary to Part I. of the *Essai*, he says: 'The chemical qualities of

<sup>1</sup> *Essai*, 1. 59—60.

<sup>2</sup> *Essai*, 1. 36—37.

<sup>3</sup> *Essai*, 1. 37. A theory of solution, closely resembling that of Berthollet, has been proposed by W. W. J. Nicol: see *Phil. Mag.* (5) 15. 91.



different substances depend (1) on their tendencies to combine, whereby they mutually saturate each other, and which tendencies remain more or less dominant in the compounds produced; (2) on their relations to heat, which modify their combining powers, by causing variations in the quantities of the substances coming within the spheres of mutual action, and also by opposing elasticity (*élasticité*<sup>1</sup>) to condensation, the latter of which is one of the effects of combination; (3) on the mutual actions of their small particles (*molécules*<sup>2</sup>), acting in the same direction as the affinity which has produced combination, but opposed to actions and reactions between these particles and those of other substances; (4) on their relations to other substances, which combine with them, but not so as to produce a mutual saturation (*saturation*<sup>3</sup>), but rather a division and varying distribution of properties, and chiefly of those properties which depend on the constitution (*constitution*<sup>4</sup>).

174. Davy, as we found in book I. (chapter II. par. 46), regarded chemical and electrical effects as probably due to the same cause, certain mutual relations between small particles of matter producing effects called chemical, as certain mutual relation between masses of matter produce effects called electrical. Davy regarded a fixed chemical system as stable because of the balance of chemical and electrical forces; contact of the metals [in the galvanic pile] destroys electrical equilibrium, and chemical changes restore it again, and in consequence the action [of the pile] exists as long as the decompositions continue.

<sup>1</sup> *Élasticité*. Berthollet uses this word as meaning nearly the same as *dilatation*, or perhaps we might now say *disgregation*. (See chap. III. par. 239, foot-note.)

<sup>2</sup> *Molécules*. This word as employed by Berthollet means only a small particle; I have thought it better not to use the term *molecule*, as this is now employed with a more definite meaning than *small particle*.

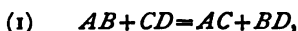
<sup>3</sup> *Saturation*. By *saturation of properties* Berthollet means that merging of the properties of the constituents in those of the new compound which is so characteristic of chemical change.

<sup>4</sup> *Constitution*. The *constitution* of a substance is conditioned according to Berthollet by its condensation and dilatation: 'the properties which depend on the constitution' of a substance may be taken as meaning, broadly, the physical properties of the substance.

175. The picture of a chemical reaction which Berzelius formed for himself was essentially based on the conception of equilibrium resulting from the actions and reactions of chemical and electrical forces. Each elementary atom was, for him, endowed with definite quantities of positive and negative electricity, but each atom was nevertheless essentially unipolar. The strivings of atoms to neutralize their opposite electricities is measured by the intensity of the unipolarity of each. This striving is what Berzelius called chemical affinity.

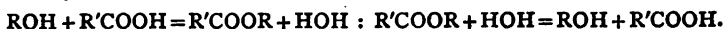
These great chemists were agreed in regarding the object of chemistry to be an explanation of the changes which matter undergoes; they did not think that the ability to give an account of the physical properties of each kind of matter sufficed to make one a chemist. Chemical change was, for them, continuously proceeding, but it might be checked by the action of electrical, or thermal, or other forces. Their fundamental conception is clearly that of an equilibrium resulting from the actions of different forces, the principal of which are chemical, electrical, and thermal.

176. Little was done to advance the study of chemical change until comparatively recent times. In 1867 Guldberg and Waage published their most important memoir *Études sur les Affinités Chimiques*. These naturalists, whose work we must study carefully in another chapter, have paid attention chiefly to changes which are reversible and which belong to the general type represented by the two equations<sup>1</sup>:



The cycle consists of two parts, (1) the direct change, (2) the reverse change; it presents analogies with dissociation<sup>2</sup>.

<sup>1</sup> An instance of such a reversible change is furnished by the action of alcohols on acids,



Van't Hoff proposes the notation



for reversible changes. (*Études de Dynamique Chimique* [1884], p. 8.)

<sup>2</sup> See *ante*, pars. 171, 172.

If  $AB$ ,  $CD$ ,  $AC$ , and  $BD$  are all in the same physical state, say are all gases, the direction and amount of the change will be chiefly conditioned by chemical forces; but if one of these bodies is a solid or liquid, if one is more insoluble in the menstruum present than the others, if one is more compact than the others, &c., then the amount and direction of the change will be more or less conditioned by what Guldberg and Waage call secondary forces. One principal object of the *Études* is to eliminate the influence of secondary forces, and so to arrive at relative measurements of the chemical forces which condition chemical changes, in other words, to gain relative measurements of chemical affinities.

177. But we are not yet in a position to discuss the work of the Norwegian naturalists from this point of view. At present we are endeavouring to gain a general view of the conditions and the course of chemical actions. Now there are many groups of facts which must some day find their place in a general theory of chemical action, but which lie scattered, in a more or less casual way, over the pages of chemical memoirs; the more important of these facts may be roughly classified under the following four heads: (1) contact-actions; (2) predisposing affinity; (3) induction; (4) influence of mass.

I wish now to illustrate each of these groups of facts.

178. *Contact-actions*<sup>1</sup>. When a mixture of sulphur dioxide and oxygen is passed over hot finely-divided platinum the gases combine to form sulphur trioxide, but the platinum is unchanged at the end of the reaction. Ozone is decomposed by contact with metallic silver, while the silver is itself unchanged. When acetylene is heated in a closed tube over mercury it is gradually changed into a mixture of benzene, cinnamene, naphthalene, &c., but if a piece of recently heated coke is introduced into the tube, the acetylene is almost wholly changed into carbon and hydrogen, while the coke is itself unaffected<sup>2</sup>. When sulphur dioxide and chlorine are passed into a little camphor, much sulphuryl chloride ( $\text{SO}_2\text{Cl}_2$ )

<sup>1</sup> Called also *catalytic actions*.

<sup>2</sup> Armstrong and Groves, *Organic Chemistry*, 211 (quoting Berthelot).

is produced, and the camphor is unchanged at the close of the action; but chlorine has no action on liquid sulphur dioxide, nor does it act upon camphor under the conditions which exist in the formation of sulphuryl chloride. Some other substances which absorb sulphur dioxide, e.g. alcohol, acetone, sulphur trioxide, &c., do not bring about the formation of sulphuryl chloride when brought into simultaneous contact with sulphur dioxide and chlorine<sup>1</sup>.

In these, and other similar changes, one of the necessary components of the changing system apparently remains unaltered throughout the entire reaction. There are other chemical changes which occur only in presence of a substance which is itself unaltered at the close of the reaction, but which can be proved to undergo a cycle of changes, through which it continuously passes and repasses, during the progress of the main chemical process. Thus the presence of a little aluminium chloride renders possible many reactions among carbon compounds which do not proceed in the absence of this substance; benzoic acid, for instance, is produced by passing dry carbonic anhydride into hot benzene containing a little aluminium chloride; and benzene-sulphinic acid is produced when the hydrocarbon is treated, under similar conditions, with sulphurous anhydride. Bleaching powder is wholly decomposed, yielding calcium chloride, oxygen, and water, by heating with a relatively very small quantity of cobaltous oxide. It has been shewn that the aluminium chloride in one case, and the cobaltous oxide in the other, is continuously changed and reproduced during these chemical actions.

There are other actions which appear to be commenced by the presence of small quantities of substances which afterwards take no part in the action. Thus Wanklyn<sup>2</sup> found that dry sodium, even when fused, does not combine with dry chlorine, but that if a trace of moisture is present the action begins, and readily continues. Dixon<sup>3</sup> has also shewn, that a mixture of perfectly dry carbon monoxide and oxygen

<sup>1</sup> Schulze, *Journal für prakt. Chemie*, (2) 24. 168.

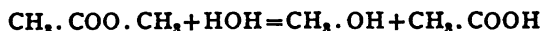
<sup>2</sup> *Chem. News*, 20. 271.

<sup>3</sup> *Nature*, 28. 551.

is not exploded by the electric spark, but that the addition of a minute quantity of water causes the gases to combine quietly when submitted to the action of the electric spark, and that explosion occurs when the gases are moist.

Several of these so-called contact-actions are certainly to be placed in the same class as ordinary chemical changes, and any explanation which may be given of chemical action must include these as special cases. Other contact-actions, e.g. those of spongy platinum, are more physical than chemical, and in so far as this is so, they must be classed with those physical phenomena which probably form part of every complete cycle of chemical change.

The remaining instances of contact-actions are probably to be included in the general theory of the influence exerted by changes in the relative masses of the reacting bodies on the course of chemical reactions. That this is so, in some cases at least, has been shewn by Ostwald, in his study of the variation produced in the velocity of the process represented by the equation



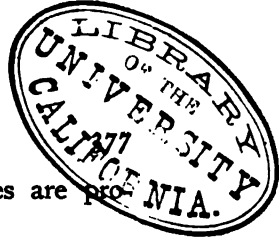
by the presence of various acids which take no direct part in the chemical reaction<sup>1</sup>.

179. *Predisposing affinity.* Such a chemical change as the following not unfrequently occurs. If the compound  $AB$  were decomposed by the body  $C$ ,  $AC$  and  $B$  would be produced; this decomposition does not however take place except in the presence of a third body  $D$ , which is known to form a compound with  $B$ , viz.  $BD$ . The initial configuration of the system is represented by  $AB, C, D$ ; the final configuration by  $AC, BD$ .

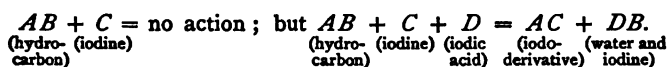
The substance  $D$  was said by Berzelius to exert a predisposing affinity on  $B$ .

Thus, iodine does not act on the hydrocarbons, as a group,

<sup>1</sup> *Journal für prakt. Chemie*, (2) 28. 449. This paper will be referred to in more detail in chap. III. par. 224.

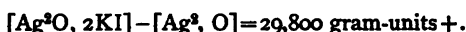


to produce iodo-derivatives, but these derivatives are produced by the joint action of iodine and iodic acid,



Again, sulphur dioxide, oxygen, and water very slowly react to produce sulphuric acid, but if these three substances are brought into contact with sodium chloride at about  $400^{\circ}$ , sodium sulphate is rapidly produced; the sodium chloride appears to act upon the potentially formed sulphuric acid with production of sodium sulphate and hydrochloric acid.

In these actions it is probable, or indeed almost certain, that the reaction  $AB + C = AC + B$  does occur to a very small extent in the absence of the third body  $D$ , and that the subsequent reaction between  $B$  and  $D$  is attended with the setting free of a considerable quantity of energy which is used in doing chemical work represented by the primary change  $AB + C = AC + B$ . That this is so in some cases is rendered evident by Berthelot's and Ditte's measurements of the quantities of heat evolved during the oxidation of mercury and silver, and during the conversion of the oxides so formed into chlorides and iodides. These measurements shew that much more heat is evolved during the latter, than during the former reactions; thus,



Now silver is not oxidised by dry or moist oxygen, but silver oxide is rapidly converted into iodide by immersion in a dilute solution of potassium iodide; moreover silver is itself easily changed into silver iodide by the action of the same solution; it is very probable that in the last-named change silver oxide is produced but is at once decomposed with formation of silver iodide and caustic potash<sup>1</sup>.

Another instructive instance of the action of the so-called *predisposing affinity* is furnished by the change of the amides of the acetic acid series into ammonium salts of the same acids.

<sup>1</sup> Ditte, *Compt. rend.* 93. 415. See also Berthelot, *Bull. Soc. chim.* (2) 35. 487.

The change  $\text{RCONH}_2 + \text{HOH} = \text{RCOONH}_2$  proceeds very slowly; but if an acid, e.g.  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , &c. &c. is added, the change proceeds rapidly, each acid exerting its own specific action in accelerating the process, and in determining the limits at which the process stops for given conditions of temperature and dilution. As we shall learn hereafter, the action of the acids in this change is in all respects a normal one, and the entire process belongs to the ordinary type of chemical change<sup>1</sup>.

180. *Induction.* When a mixture of hydrogen and chlorine is exposed to sunlight hydrochloric acid is rapidly formed. Bunsen and Roscoe<sup>2</sup> noticed that when a mixture of these gases in equal volumes is kept for some time in the dark, and is then exposed to light, an appreciable time elapses before any chemical action begins, and that the velocity of the action increases, at first slowly, then more rapidly, until a maximum is reached, after which it decreases. If the reaction is allowed to begin and the mixture is then placed in the dark, the process stops, and on again bringing the mixed gases into sunlight the same course is gone through as before. The greater the intensity of the light the shorter the time which elapses before the maximum action is reached. If a very minute trace of oxygen, or even a slight excess of hydrogen, is added to the mixture of chlorine and hydrogen, a longer time elapses before the maximum action is reached, than if a mixture of the pure gases in equal volumes is used; indeed the total amount of action seems never to be so great in the former as in the latter case. Hence a minute quantity of oxygen acts, in some way, in decreasing the velocity of the change  $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$ .

Bunsen and Roscoe speak of the mixture of hydrogen and chlorine as exhibiting a resistance to chemical change; 'induction' is the act of overcoming this resistance.

Wright<sup>3</sup> noticed the occurrence of a similar phenomenon in the reduction of metallic oxides by carbonic oxide and

<sup>1</sup> See *post*, chap. III. par. 222.

<sup>2</sup> *Phil. Trans.* for 1857. 355.

<sup>3</sup> *C. S. Journal Trans.* for 1879. 475; *do.* for 1880. 757 (see especially p. 790).

hydrogen. An appreciable time elapsed before any action could be observed, the rate of action then slowly increased, then more rapidly increased to a maximum, after which it decreased. A curve which shall represent these results will have (roughly) this general form (figure 1), whereas the

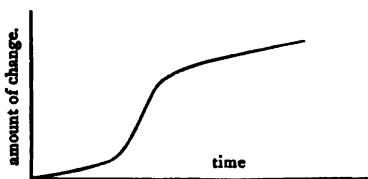


FIG. 1.

curve representing a normal process of dissociation has the general form shewn in figure 2.

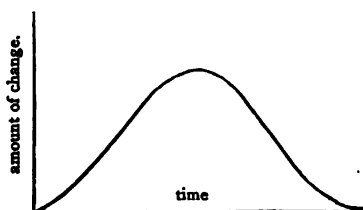


FIG. 2.

The phenomenon was more marked, in Wright's experiments, when the reduction was accomplished by means of carbonic oxide than when hydrogen was the reducing agent; the changes in the velocity of the action were also more noticeable at medium, than at very high or very low temperatures.

It is not, it seems to me, necessary to make use of any special term indicative of a difference of kind between these and other chemical changes.

Wright has shewn that the observed variations of the rate of the reactions are largely dependent on secondary changes, and on the physical state of the metallic oxides employed. These reactions are but fresh illustrations of the fact we so easily forget that every chemical change is a complex occurrence. The formation of hydrochloric acid from hydrogen and chlorine is not so simple as the equation  $H_2 + Cl_2 = 2HCl$



represents it to be. The course of the reaction is considerably modified by the presence of minute quantities of other substances, because such minute quantities further complicate the primary change. We have here an instance of the influence of *secondary forces* on a chemical reaction. Almost every chemical change must, it would appear, consist of several parts, one of which may be regarded as primary and the others as secondary. 'Induction' therefore becomes an essential feature of all chemical processes. But we do not require a special term. Many circumstances may occur to prevent the attainment by a changing system of what we may call its normal equilibrium. But this condition is finally attained. The striving towards this state is not a special feature of a few reactions, but is an essential part of all reactions. Small alterations of the conditions under which a change proceeds may much retard the attainment of the final equilibrium; e.g. lowering the temperature<sup>1</sup>, or even such mechanical actions as greater or less agitation, or removing part of the changing system from the rest of the system<sup>2</sup>.

If a new compound is introduced into the changing system the rate of change must, we should think, be varied, the new substance exerting either a positive or a negative accelerating effect<sup>3</sup>; but if the normal state is attained in the long run,

<sup>1</sup> Lowering temperature may act either physically, by decreasing the molecular motions and hence the chances of decomposition in a given time, or chemically, by bringing about the formation of complex molecular groups. An example of both actions has been worked out to some extent by the author (*C. S. Journal Trans.* for 1880. 78. See also Potilitzin on the formation of hydrates of cobaltous chloride; *Ber.* 17. 276).

<sup>2</sup> When one or more of the constituents of a chemical system is gaseous, alterations of pressure will considerably modify the direction of the change and the final configuration of the system; thus a solid hydrate  $\text{CO}_2 \cdot x\text{H}_2\text{O}$  may be formed by compressing  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , and there appears to be a definite pressure for each temperature at which the hydrate is produced. Probably  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ,  $\text{CS}_2$  and  $\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_2$  and  $\text{H}_2\text{O}$ , &c., form a series of hydrates which are decomposed and re-formed according to changes of temperature and pressure: see Dewar, *Proc. R. S.* 30. 538; Wroblewski, *Compt. rend.* 94. 212, also *Wied. Ann.* 17. 103; Cailletet and Bordet, *Compt. rend.* 95. 58. For confirmatory evidence of a more directly chemical nature, see Ballo, *Ber.* 15. 3003.

<sup>3</sup> See Harcourt and Esson, *C. S. Journal*, 20. 460. This paper will be considered in section 2 of this chapter. See par. 196.

we shall have the phenomenon called by Bunsen and Roscoe *induction*. It is very easy to overlook parts of a chemical change; one is apt to pay attention only to the initial and final states of the system. Induction may thus occur and not be noticed<sup>1</sup>.

181. *Influence of mass.* If it is admitted that the course of a chemical change may be considerably modified, or even completely altered, by altering the conditions under which the change proceeds, we should, I think, expect to find that varying the relative masses of the reacting bodies would be one of the commonest ways whereby such modification or alteration might be effected. We have learned what importance Berthollet attached to the relations between the masses of substances taking part in a chemical process, and we have seen in book I. that attention must be paid to these relations in discussing the data of thermal chemistry, even when the questions under consideration rather concern the composition than the actions of the various compounds.

Recent years have witnessed the publication of many important researches on the subject of mass-action; I shall deal with Guldberg and Waage's work in some detail hereafter, at present I wish only to insist on the importance of considering the relative masses of the reacting bodies in all processes of chemical change, and to remind the student that this factor is almost universally ignored in our ordinary chemical equations<sup>2</sup>.

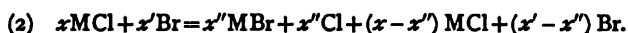
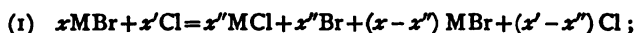
When sodium (or potassium) sulphate, and sulphuric acid, are allowed to react in equivalent quantities in the presence of water, the relations between the masses of  $\text{Na}_2\text{SO}_4$ ,  $\text{NaHSO}_4$ , and  $\text{H}_2\text{SO}_4$ , found in the solution at any given temperature are conditioned by the mass of the water present. There is probably direct mutual action between the water and the  $\text{NaHSO}_4$ , with production of  $\text{H}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$ , the reverse change being brought about by the

<sup>1</sup> The chemical changes of the carbon compounds furnish innumerable instances of the importance of observing the intermediate steps in these changes.

<sup>2</sup> An interesting paper on this subject by J. Morris, giving references to all the more important memoirs, will be found in *Annalen* 212. 253.

$\text{H}_2\text{SO}_4$  which has been added. If an excess of  $\text{Na}_2\text{SO}_4$  is added, the amount of water being large and remaining constant, a greater quantity of  $\text{NaHSO}_4$  remains unchanged to  $\text{Na}_2\text{SO}_4$  than if an equivalent excess of  $\text{H}_2\text{SO}_4$  is added. That is to say, the action of  $\text{Na}_2\text{SO}_4$  is modified by the presence of the water in a way different from that in which the action of  $\text{H}_2\text{SO}_4$  is modified; or, to put this statement in another form, the affinity between  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  is not the same as the affinity between  $\text{Na}_2\text{SO}_4$  and  $\text{H}_2\text{O}$ <sup>1</sup>.

Potilitzin's investigations of the influence exerted by variations in the masses of the acting bodies on the reactions which occur between the halogens and various metallic haloid salts have already been referred to (book I. chap. IV. par. 131). It is well known that metallic bromides are decomposed by chlorine, but Potilitzin has shewn that the reverse change also occurs at moderate temperatures. The two processes may be represented thus,



Potilitzin's results teach us that when  $x'$  is increased in (2), the amount of  $\text{MBr}$  formed also increases, up to a certain limit, whereat equilibrium is established. The same chemist has more recently examined the reactions between silver chloride (and bromide), and metallic bromides and iodides in aqueous solutions at ordinary temperatures<sup>2</sup>.

The various changes may be represented thus,



In any case the amount of action is dependent, among other conditions, on the relative masses of the reacting bodies. In these, as in his earlier experiments, Potilitzin finds that a condition of equilibrium is attained, after a time, by the

<sup>1</sup> For more details see Ostwald, *Journal für prakt. Chemie* (2) 23. 305. For older investigations of the modifying influence of water on various changes, see H. Rose, *Pogg. Ann.* 82. 545.

<sup>2</sup> See abstract in *Ber.* 16. 3051.

distribution of the halogens between the silver and the metal of the haloid salt<sup>1</sup>.

182. From what has been said in the preceding paragraphs (178-181), we see that a changing chemical system may pass through a series of stages some of which are more stable than others. It may indeed be that certain points in the series are so unstable that they are not marked by the production of what we are accustomed to call definite chemical compounds<sup>2</sup>. This view, of well marked chemical compounds being the most stable points in a series of potentially existent substances, has been developed by Mills, starting from the observations of Wurtz on the polyethylenic glycols, which are compounds obtained by the condensation of  $n$  molecules of ethylene glycol with the elimination of  $n - 1$  molecules of water. Mills uses the expression *cumulative resolution*<sup>3</sup> to mean 'the combination of a substance or mixture of substances with itself  $n$  times, a particular portion of it 'being lost each time, according to some fixed law.'

The general equation representing a process of cumulative resolution is given by Mills in this form,

$$nA_aB_\beta C_\gamma \dots - (n - m) A_aB_bC_c \dots = A_{m(a-a)} + m_a B_{(\beta - b)} + m_b C_{(\gamma - c)} + m_c ;$$

where  $A_aB_\beta C_\gamma$  is the substance which undergoes the change, and  $A_aB_bC_c$  is that portion of it which is eliminated at each stage of the process. By giving values to  $n$  varying from

<sup>1</sup> For a fuller discussion of the influence of mass on chemical changes see *post*, chap. III. section 1.

<sup>2</sup> It should be noted that the expressions 'stability,' 'stable compound,' and the like, are somewhat vague. The conditions under which stability is predicated of a given substance must be stated or implied if the word is to convey any very definite meaning. Thus zinc methide can be gasified without decomposition, but when this compound is brought into contact with water it is violently decomposed, forming zinc hydrate and methane; so also the compound  $K_2O_4$  is decomposed at a red heat, yielding  $K_2O + O_2$ , but it is rapidly acted on by water at ordinary temperatures, forming  $KOH$ ,  $O_2$  and  $H_2O_2$ . The fact that some double salts are decomposed in aqueous solutions by the process of diffusion, seems to illustrate the position that certain molecules, or molecular groups, which shew a considerable range of what may perhaps be called chemical stability, are easily broken up when small alterations are made in the physical conditions of their surroundings.

<sup>3</sup> See *Phil. Mag.* (5) 3. 492; or the article 'Cumulative resolution,' in the third supplement of Watts's *Dictionary*.

0 to  $\infty$  various formulæ are obtained for the *cumulates*, or possible products of the change. The theory may be applied to the action of water on bismuthic nitrate, whereby a series of compounds is obtained, each less nitrogenous and more bismuthic than the preceding. Thus,

$$\pi (\text{Bi}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5) - (\pi - 1) \text{N}_2\text{O}_5 = \text{Bi}_{2\pi}\text{O}_{3\pi} \cdot \text{N}_{4\pi+2}\text{O}_{10\pi+5};$$

by giving various values to  $\pi$  from 0 to  $\infty$  we obtain the formulæ of all possible substances between  $\text{Bi}_2\text{O}_3 \cdot 3\text{N}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5$ . By repeating this process on  $\text{Bi}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5$ , a series of possible substances is obtained of which the limits are marked by  $\text{Bi}_2\text{O}_3 \cdot 2\text{N}_2\text{O}_5$  and  $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$ ; and lastly by a repetition of the process of cumulative resolution on the last compound, a third series is obtained ranging from  $\text{Bi}_2\text{O}_3 \cdot \text{N}_2\text{O}_5$  to  $\text{Bi}_2\text{O}_3$ <sup>1</sup>.

183. This theory points to the frequent existence of series of substances forming connecting links between those comparatively stable compounds which can be separated from the materials which have produced them, or from those which are the products of their decomposition.

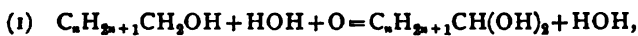
But although we may not be able to separate and obtain in definite form the comparatively unstable members of such series, yet it may be possible to demonstrate the existence of these substances by indirect methods.

The substances in question exist only as members of a system; apart from the other members, or from some of the other members, they undergo decomposition.

The group of carbon compounds called by Armstrong and Groves *Aldehydrols*<sup>2</sup> presents us with examples of the phenomenon now under consideration. Aldehydrols are almost certainly produced in the first stage of the oxidation of the primary ethylic alcohols. These alcohols are oxidised only in presence of water; for this and other reasons it is very probable that the process of oxidation is represented by the equations

<sup>1</sup> For other applications of the theory see the article in Watts's *Dict.*

<sup>2</sup> *Organic Chemistry*, 1. 504.



where  $\text{C}_n\text{H}_{2n+1}\text{CH}(\text{OH})_2$  is the formula of an aldehydrol<sup>1</sup>.

Many reactions of the ethylic aldehydes are explained by assuming the existence of aldehydrols<sup>2</sup>; the properties of chloral hydrate point almost with certainty to the formula  $\text{CCl}_3 \cdot \text{CH}(\text{OH})_2$  for this compound<sup>3</sup>.

The aldehydrols cannot however exist except as members of a system of which water is a constituent; the system is chemically stable, some of the individual members when separated from the others are very unstable.

Another illustration of the existence of a compound only in the presence of others is furnished by Traube's preparation of cupric iodide ( $\text{CuI}_2$ ) in aqueous solution. An aqueous solution of this compound, the supposed non-existence of which has been often noticed as peculiar, can be prepared according to Traube by mixing dilute solutions of cupric sulphate and potassium iodide, or by acting on cuprous iodide ( $\text{Cu}_2\text{I}_2$ ) with iodine in the presence of a large quantity of warm water<sup>4</sup>.

184. Looking back on the conception of molecular structure which was reached in book I. (par. 64 *et seq.*), and applying to it the further knowledge we now have, we should be inclined to say that the function performed by a given atom, or group of atoms, in this molecule or in that cannot be known except by the study of many systems wherein the given individual occurs. Before we have a knowledge of the chemical properties of hydrogen, for instance, we must study the behaviour of this element, under varying conditions, in its compounds with metals, with nonmetals, with negative and with positive groups of atoms, &c. It might indeed be asserted that it is not correct to say that the molecule of

<sup>1</sup> See Armstrong and Groves, *loc. cit.* 1. 417—418.

<sup>2</sup> *Ibid. loc. cit.* 717—718. See also p. 681 (formation of acetal from ethaldehyde).

<sup>3</sup> Compare the properties and formation of chloral hydrate (*ibid.* pp. 743—744) with the properties of chloral alcoholate (*ibid.* p. 429).

<sup>4</sup> *Ber.* 17. 1064.

water contains hydrogen or oxygen, just as it is not correct to say that the molecule of sulphuric acid contains the atomic groups  $\text{SO}_2$  or  $\text{H}_2\text{O}$ . Mills<sup>1</sup> goes so far as to affirm that water is not represented by the formula  $\text{H}_2\text{O}$ , inasmuch as it is a homogeneous substance with its own properties; to this we might, I think, reply that one of the distinctive properties of water is implied in the formula  $\text{H}_2\text{O}$ , the property namely of being decomposable into  $\text{H}_2$  +  $\text{O}$ , and of being formed by the combination of  $\text{H}_2$  and  $\text{O}$ .

Every chemical substance ought to be regarded in its relations to other substances; but each is also a distinct individual. A full chemical knowledge of any substance implies a knowledge of all the possible reactions which would occur in any system of which that substance may form a member. The whole history of dualism warns us against asserting that the properties of any chemical substance are independent of those other substances with which it is or may be associated; but at the same time, all modern research confirms the fundamental conception of the element as a distinct form of matter which impresses its own likeness on all the compounds of which it forms a constituent.

## SECTION II. *Chemical Equilibrium.*

185. Thus we come back to the conception of every chemically stable system as being in a condition of equilibrium, which is the result of the actions of various forces, some of which are what we usually call chemical, and others physical; if one of these forces is increased the equilibrium is overthrown and the system undergoes chemical change.

The methods used in attempts to solve the general problem of chemical equilibrium may be divided into two classes, (1) those which are based on applications of the molecular theory, and more especially on the kinetic theory of gases; (2) those which are essentially thermodynamical.

<sup>1</sup> *Phil. Mag.* (5) 1. 1.

186. Several years ago Williamson<sup>1</sup> put forward a somewhat vague view, to the effect that the amount of chemical action between two substances may be measured by the relative velocities of the atomic interchanges taking place between the molecules of these substances.

Arguing from the reactions of substitution among carbon compounds, especially the substitution of H in  $H_2SO_4$  by  $C_nH_{2n+1}$  groups and *vice versa*, Williamson concluded, that if chemically similar atoms continually change places in reacting molecules, much more likely is it that chemically identical atoms will undergo intermolecular change. 'We are thus forced to admit that in an aggregate of molecules of any compound there is an exchange continually going on between the elements which are contained in it.' In a drop of an aqueous solution of hydrochloric acid, for instance, 'each atom of hydrogen is constantly changing places with other atoms of hydrogen'; when a solution of copper sulphate is added to hydrochloric acid, then the interchange of copper for copper, and of hydrogen for hydrogen, proceeds as before, but in addition to this 'the hydrogen does not merely move from one atom of chlorine to another, but in its turn also replaces an atom of copper, forming chloride of copper and 'sulphuric acid.' When one product is insoluble it is removed, and so almost the whole of one of the original substances is decomposed.

187. Pfaundler<sup>2</sup> has developed a hypothesis somewhat similar to that put forward by Williamson. Pfaundler's hypothesis is indeed grounded on the second law of thermodynamics, but its development proceeds on the lines of the molecular theory.

Let there be two gases,  $AB$  and  $CD$ , formed from  $A$ ,  $B$ ,  $C$  and  $D$ , with the evolution of less heat than that which accompanies the formation, from the same constituents, of two other gases,  $AD$  and  $BC$ ; then the change from  $AD$ ,  $BC$  back to  $AB$ ,  $CD$  will necessarily be attended with absorption

<sup>1</sup> *C. S. Journal*, 4. 110—112. (See also *do.* 4. 229; also *Phil. Mag.* (3) 37. 350.)

<sup>2</sup> *Fogg. Ann. Jubelhd.* 182: and *do.* 131. 55 *et seq.* (especially pp. 66—71).



of heat. In other words the reverse operation, thermally considered, will be a negative change, and it must be accompanied by a compensating positive change.

Let heat pass from a hotter body to the mixture of  $AD$  and  $BC$  molecules, then this addition of heat (i.e. this positive change) *may* be accompanied by an equivalent, or less than an equivalent, negative change; the re-formation of  $AB$  and  $CD$ , or generally an action involving absorption of heat, *may* occur.

Suppose that in a given space there is a limited number of molecules  $AB$ ,  $CD$ ,  $AD$ , and  $BC$ , that no heat enters or leaves the system, and that the temperature of the space remains constant; then a series of molecules may be produced, represented by the formulæ  $AC$ ,  $BD$ ,  $AA$ ,  $BB$ ,  $CC$ ,  $DD$ ,  $\left\{ \begin{smallmatrix} AC \\ BD \end{smallmatrix} \right\}$ ,  $\left\{ \begin{smallmatrix} AA \\ BB \end{smallmatrix} \right\}$ ,  $\left\{ \begin{smallmatrix} AA \\ CC \end{smallmatrix} \right\}$ ,  $\left\{ \begin{smallmatrix} BB \\ CC \end{smallmatrix} \right\}$ ,  $\left\{ \begin{smallmatrix} BB \\ DD \end{smallmatrix} \right\}$ , &c. But according to the hypothesis already made, the production of  $AA$ ,  $BB$ ... $DD$ , must be accompanied by an absorption of heat. The formation of the elementary molecules,  $AA$ , &c. would require the greatest absorption of heat; on the other hand, the formation of the complex molecules  $\left\{ \begin{smallmatrix} AB \\ CD \end{smallmatrix} \right\}$ , &c. will, as a rule, be attended with evolution of heat. If molecules are formed with heat-absorption, such changes must be accompanied by others wherein equivalent quantities of heat are evolved.

Pfaundler then gives a rough classification of these positive and negative thermal changes<sup>1</sup>.

The relations between the distribution of the energy and the distribution of the molecular configurations in such a system are considered in Pfaundler's second paper.

The hypothesis asserts that exchange of atoms, or atomic groups, is constantly proceeding in chemical systems; but the consideration of this withdrawal and replacement of atoms, from and in the molecules of the reacting substances, can be approached only by statistical methods. There may be more withdrawals than replacements of individual atoms,

<sup>1</sup> See *Pogg. Ann. Jubelbd.* 187—8.

but, when equilibrium is established, the mean number of each in a given time is equal.

But why do exchanges of parts of molecules occur? Pfaundler's hypothesis refers these atomic exchanges to momentary differences in the states of motion of individual molecules, which is a fundamental point in the kinetic theory of gases.

Consider the motion of agitation of the molecules, and the motion of the parts of the molecules; the kinetic theory asserts that, at a constant temperature, the sum of the kinetic energies of these two motions is constant, and also the sum of each is constant, but the two motions may be very differently distributed among the individual molecules. Calling the energy of agitation of the molecules of a system (*a*), and the energy of rotation of the parts of the molecules (*b*), there are four limiting cases for the distribution of these two energies.

- Case 1: (*a*) and (*b*) are both at a maximum;  
„ 2: (*a*) and (*b*) are both at a minimum;  
„ 3: (*a*) is at a minimum, and (*b*) at a maximum;  
„ 4: (*a*) is at a maximum, and (*b*) at a minimum.

Pfaundler illustrates these four cases as follows:

(1) Two molecules, *AB* and *CD*, collide, so that at the next instant (*a*) is wholly or almost wholly changed to (*b*); therefore (*b*) is greater than the maximum for stability in both molecules. The molecules *AB* and *CD* separate into *A*, *B*, *C*, and *D*.

(2) Two molecules, *AB* and *CD*, collide; it is possible that the resulting internal motion of the parts of the molecules is too small to separate *AB* and *CD* into their constituents; but is also too small to prevent the formation of the complex molecule *ABCD*, which is therefore produced.

(3) After collision the resulting internal motion is too small to separate *AB* and *CD* into their constituent parts, but is sufficient to prevent the formation of *ABCD*; the original molecules, *AB* and *CD*, therefore rebound unchanged.

(4) The complex molecule  $ABCD$  is momentarily formed; but the blow of  $AB$  on  $CD$  being, according to the simplest hypothesis, direct and central, the whole system vibrates. Whether  $ABCD$  shall separate into  $AB$  and  $CD$ , or into  $AC$  and  $BD$ , depends on the magnitude of the affinities of  $A$ ,  $B$ ,  $C$ , and  $D$  for each other, and also on the previous internal motions of the parts of  $AB$  and  $CD$ ; the greater this internal motion, the more readily will the change now proceed in the direction of  $AC$  and  $BD$ , because the further will the separation of  $A$  from  $B$ , and of  $C$  from  $D$ , have been already carried.

Hence, Pfaundler concludes, the nature (*Art*) of a decomposition depends on the mutual affinities of the constituents of the system, and also on the conditions of motion of these constituents; reactions may occur in directions apparently opposed to the affinities.

Cases (3) and (4) will probably occur more frequently than cases (1) and (2), because the former require smaller differences between the motions of the individual molecules than the latter.

Remembering that the kinetic energy of the atoms in the various molecules may be associated with many kinds of motion (swinging motions, rotations, &c.), one recognises how manifold may be the possible distributions of molecular configuration. The molecules may undergo many changes (the mean temperature of the system remaining constant) which we should regard as departures from a normal condition obtaining if all the molecules were simultaneously in the same state. The simplest of such departures from the average state is exhibited by the processes of dissociation, which is however only a special (although the simplest) case of 'simultaneous reciprocal reactions in consequence of variations in the motions of individual molecules<sup>1</sup>'.

<sup>1</sup> Pfaundler devotes some space to considering the best name to give to the general phenomenon of which he says dissociation is a special case; he finally adopts the expression 'competition (*concurrens*) of the molecules' (see *Pogg. Ann. Jubelbd.* 189). This theory of chemical change developed by Pfaundler is not opposed to the results of recent electrical investigations regarding chemical affinity; see *post*, chap. III. par. 252.

188. The hypothesis of Pfaundler indicates that there must be a temperature at which any given chemical change begins, and that for every temperature there is a limit beyond which the change does not proceed. Only a few determinations have as yet been made of the limiting conditions of chemical operations, and of the rates at which the operations proceed within these limits.

Menschutkin's experiments on the rates and limits of etherification<sup>1</sup>, which have been partly considered in book I., and more especially Ostwald's studies of the velocities of various chemical changes<sup>2</sup>, furnish examples of the kind of work that is required<sup>3</sup>. [For a few examples of such investigations see *post*, pars. 195—199.]

189. Pfaundler's treatment of chemical equilibrium throws some light on the questions of nascent actions discussed from the statical point of view in book I. (chap. II. section 1). These actions may I think be treated as special instances of equilibrium coming under Pfaundler's case (4) [see *ante*, p. 389]. If we grant that when hydrogen, for instance, is evolved by the action of zinc on dilute sulphuric acid, the gas consists for a short but appreciable time for the most part of atoms (or monatomic molecules), then we have a system wherein the motion of rotation of the parts of one kind of the molecules *AA* (or *BB*) is so great that most of these molecules are actually separated into their constituent parts *A*, *A* (or *B*, *B*); hence, if there be within the sphere of action another set of molecules, *CD*, the change will proceed in the direction indicated by the formation of the new molecules *AC* and *AD*. If however the energy due to the separation

<sup>1</sup> See *ante*, book I. chap. IV. pars. 157—8; also *post*, par. 197.

<sup>2</sup> See *post*, chap. III. par. 222.

<sup>3</sup> Hood's experiments (*Phil. Mag.* (5) 6. 371) on the oxidation of ferrous sulphate solution by potassium chlorate led to the probable conclusion that the amount of chemical change varied as the square of the temperature. Warder (*Amer. Chem. Journal*, 3. No. 5) has arrived at the same conclusion from his study of the influence of temperature, &c., on the rate of saponification of ethylic acetate. Mills and Mackey (*Phil. Mag.* (5) 16. 429) have examined the relations between the strength of aqueous sulphuric acid and the line of 'no chemical change', for given temperatures, in the reaction between that acid and metallic zinc.

of  $AA$  into  $A$  and  $A$  is not employed in bringing about the secondary change, namely, formation of  $AC$  and  $AD$ , then the separated atoms swing back into their previous configuration, and the whole system assumes a new condition of equilibrium.

Moreover, whether the molecules  $AA$  (or  $BB$ ) shall, or shall not, be separated into the atoms  $A$ ,  $A$  (or  $B$ ,  $B$ ) must to a great extent depend on the materials from which, and the conditions under which, these molecules have been produced. Again, whether these monatomic molecules ( $A$ ,  $A$ ), having been produced shall react with the molecules  $CD$ , to form  $AC$  and  $AD$ , or shall swing back to the configuration  $AA$ , must be conditioned, among other things, by the nature of the molecules  $CD$ . Finally the equilibrium of the entire system will vary with variations in the rate of production of  $A$ ,  $A$ , and with variations of physical conditions, among which conditions temperature will be especially important.

190. Pfaundler shews that his hypothesis affords a fairly satisfactory explanation of many cases of *contact-action* and *predisposing affinity*<sup>1</sup>, this explanation being based on the deduction from the hypothesis in question, that the number of molecules of one kind present at any time in a changing system must depend on the nature and number of all the molecules, of whatever kind, which comprise the system.

Thus let a gaseous system consist of the molecules  $AB$ ,  $BC$ ,  $A$ , and  $C$ . Let the temperature be constant, but let the mass of  $AB$  be increased; the number of free molecules of  $C$  decreases, more of  $BC$  forms, but at the same time more molecules of  $BC$  are decomposed in a given time than before the number of  $AB$  molecules was increased.

Decreasing the amount of  $A$  will decrease the decomposition of  $BC$  by  $A$ , and hence will decrease the number of  $C$  molecules. If  $AB$  increases, and  $A$  simultaneously decreases,  $C$  will soon disappear. On the other hand it is evident that if  $AB$  decreases, and  $A$  increases, the number of molecules of  $C$  will also increase<sup>2</sup>.

<sup>1</sup> See *ante*, pars. 178, 179.

<sup>2</sup> See also Hicks, *Phil. Mag.* (5) 4. 82.

191. Dissociation appears as a particular instance of the application of Pfaundler's hypothesis of chemical equilibrium<sup>1</sup>. This subject has been treated by more purely mathematical methods by Hicks<sup>2</sup>, who has arrived at results very similar to those obtained by Pfaundler. Hicks has, it is true, failed to deduce any simple relation between the mutual atomic actions of an elementary gas and the phenomena which attend the dissociation of the molecules of that gas, but he arrives at the same general conception of a gaseous system as Pfaundler had done before, the conception, namely, of equilibrium, even the equilibrium of an elementary gas, as the result of the continual interchange of atoms, or atomic groups, between the molecules of the constituents. Hicks also points out that it may be possible to treat mathematically the questions presented by the phenomenon of the passage of the same gaseous system through various states, or phases, of chemical and physical equilibrium, one of which phases is always considerably more stable, as regards temperature at any rate, than the others.

192. In 1873 Horstmann<sup>3</sup> propounded a thermodynamical theory of dissociation which is also applicable, in its broad features, to other cases of chemical equilibrium. The fundamental position of Horstmann's theory is that the degree of dissociation of any system is conditioned by all the circumstances which determine the value of the entropy of that system. The system attains stable equilibrium when the entropy is as great as possible under the conditions. To determine the conditions under which the entropy of any dissociating system is at its maximum is therefore, according to Horstmann, to solve the problem of dissociation. The

<sup>1</sup> I have devoted considerable space to an account of Pfaundler's papers, because they contain, so far as I know, the only attempt that has been made to develop a kinetical hypothesis of chemical action in terms of the molecular theory of gases. It is however questionable whether hypotheses such as this are of much scientific value. We have no exact knowledge of the forces acting between the parts of molecules; and we know almost nothing of the mechanism whereby the energy absorbed by this or that substance is employed.

<sup>2</sup> *Phil. Mag.* (5) 4. 80 and 174.

<sup>3</sup> *Annalen* 170. 192.



'the energy of the mass divided by the quantity of the substance added is the *potential* for that substance in the mass considered.'

Clerk Maxwell defines the potential for any substance as 'the intensity with which the system tends to expel that component from its mass.'

The 'entropy of a body is a quantity such that without a change in its value no heat can enter or leave the body'; as the isothermal lines of a gas furnish a scale of temperature, so the adiabatics furnish a scale of entropy<sup>1</sup>.

Gibbs then attempts to determine the relations between the energy of homogeneous masses and the variables  $m_1, m_2, \dots m_n$ ,  $v, \phi, p, t, \mu_1, \mu_2, \dots \mu_n$ . Many different homogeneous bodies can be formed out of any set of component substances; any such body considered solely with regard to its composition and thermodynamic state is called by Gibbs a *phase* of the system considered. Two or more phases may coexist. If the stability of phase *A* is positive with regard to that of another phase, *B*, then phase *A* is stable; but if the stability of *A* is negative with regard to *B*, then phase *A* will tend to pass into phase *B*. Phase *A* may be stable in itself but may have its 'stability destroyed by contact with the smallest portion of matter in certain other phases'; certain changes may therefore be commenced by very small exciting causes<sup>2</sup>. The possible existence of unstable phases in heterogeneous systems has of course been known to chemists, although such phases have been almost entirely overlooked in chemical investigations; but we are taught by the researches of Gibbs that the conditions of existence of such phases, and their relations to stable phases of the same systems, can be deduced from the principles of the conservation and degradation of energy.

Gibbs then proceeds to find the 'fundamental equations' for ideal gases and mixtures of gases; a fundamental equation being one between the energy, entropy, volume, and component masses of a system; 'all the thermal, mechanical

<sup>1</sup> See on this subject Clerk Maxwell's *Heat*, p. 161: also 192—194 (6th ed.).

<sup>2</sup> For a fuller treatment of the 'criterion of stability' of homogeneous fluids, see Gibbs's first paper (*loc. cit.*), p. 447.



and chemical properties of a compound, so far as *active tendencies* are concerned [depend on these relations], when the form of the mass does not require consideration.'

When the energy of a mixture of gases, some of the proximate components of which can be formed out of others, has the least value consistent with its entropy and volume, we have what is called by Gibbs 'a phase of dissipated energy'; for such a phase the potentials for the proximate components must 'satisfy an equation similar to that which expresses the relation between the units of weight of these components'. Thus if the components of the system are hydrogen, oxygen, and water-gas, the potentials for these substances must satisfy the relation

$$\mu_H + 8\mu_O = 9\mu_W,$$

inasmuch as 8 of oxygen + 1 of hydrogen = 9 of water.

Dissociable gases are called by Gibbs 'gas-mixtures with convertible components'. If the general laws of ideal gas-mixtures apply to these gases, it may be shewn that the phases of dissipated energy are the only phases that can exist. An equation may be obtained for the relations of pressure, temperature, and density in such a mixture, and the results calculated by means of this equation may be compared with experimentally determined numbers. If the calculated agree with the experimentally determined results, then some of the general laws of chemical equilibrium may be deduced from the study of ideal gas-mixtures.

Take for instance the dissociation of  $N_2O_4$ ; equilibrium is established at a given temperature for the system consisting of  $N_2O_4$  and  $NO_2$ . The assumption made by Gibbs for this system is, that equilibrium is determined by the condition that its entropy has the greatest possible value consistent with the energy and the volume of the system; he thus obtains an equation between  $m_1, m_2, \dots m_n, t$ , and  $v$ <sup>1</sup>.

Gibbs compares the observed densities of the vapours of nitrogen peroxide, formic acid, acetic acid, and phosphorus

<sup>1</sup> For the development of the formula in question into a form which admits of ready application to such cases as the dissociation of  $N_2O_4$ , see Gibbs's second paper, *loc. cit.*, pp. 280—281.

pentachloride at different temperatures and pressures with the densities calculated by his formula. The agreement is on the whole very satisfactory, although there are some discrepancies, especially in the case of phosphorus pentachloride.

As an example of a system existing under special conditions in a phase beyond the limits of absolute stability, and of the sudden overthrow of the equilibrium of such a system by small exciting causes, Clerk Maxwell (South Kensington Sci. Conferences, 1876) notices the case of water, freed from air, remaining in the liquid state at a temperature much above the boiling point normally corresponding to the existent pressure, but exploding instantly it comes in contact with any gas. He also cites the equilibrium of a 37 per cent. aqueous solution of calcium chloride cooled below 37°, as described by Guthrie in his study of cryohydrates.

Many of the examples already given of contact-actions and predisposing affinity (pars. 178, 179) may serve to illustrate the influence exerted by matter in one phase when brought into contact with material systems in other phases. If the latter systems are in indifferent equilibrium, a very small external action may suffice to produce a large result, because when the equilibrium has been overthrown the components of the system are free to act and react, and a considerable chemical change may occur.

It may be possible to convert a phase of absolute stability first into one of relative instability, and then into one of absolute instability, by contact with matter in another phase, i.e. in ordinary chemical language by the action of a reagent<sup>1</sup>.

If the kinetic theory of chemical action developed by Pfaundler and others is in the main accepted, then it would appear that many, if not indeed most, chemically heterogeneous systems, the average state of which remains constant (i.e. sys-

<sup>1</sup> A mixture of marsh gas and oxygen which undergoes slow combustion at a certain temperature will explode, according to Mallard and Le Chatelier, after the expiration of a variable time which is longer the lower the temperature [see *Compt. rend.* 91. 825]. We have here probably an example of the passage from a stable phase, through a relatively unstable, to an absolutely unstable phase.

tems which are not undergoing what is usually called chemical change) are really in some one of those phases of relative instability which are easily overthrown by contact with small quantities of matter in other phases. The more complex the possible actions and reactions between the components of any chemically heterogeneous system, the more probable will be the occurrence of relatively unstable phases, and the more easily will what may be called the normal course of the chemical change be turned aside by small changes in the *magnitudes* or *intensities* of the system. 'Chemical induction' will be a marked feature of such processes<sup>1</sup>.

Molecular compounds may be regarded as systems in phases of indifferent equilibrium<sup>2</sup>.

194. The considerations regarding chemical equilibrium which have been sketched in the preceding paragraphs shew the great importance of accurate determinations of the course and rate of chemical changes. A considerable amount of work has been done in this direction, but much more regular and systematised research is needed before many generalisations can be made.

195. In 1855, Gladstone studied various reactions in which ferric salts reacted with potassium sulphocyanide, &c. in aqueous solutions, with the production of reddish coloured compounds. The amount of change was determined by measurements of the depth of colour produced<sup>3</sup>.

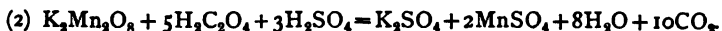
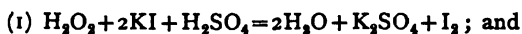
Gladstone concluded from his experiments that in chemical operations wherein all the reacting bodies and all the possible products are in solution, the rate of change depends on the rate of mutual diffusion of the various substances, and the 'coefficients of affinity' of the reacting bodies.

<sup>1</sup> When we have more data regarding the differences between the quantities of energy associated with different isomerides, it is possible that the whole theory of isomerism, regarded from the thermodynamical point of view, may be developed from the fundamental principle of equilibrium as laid down by Gibbs.

<sup>2</sup> See especially Graham's work on the colloidal and crystalloidal states of matter, more particularly his paper in *Phil. Trans.* for 1861. 183. See also many interesting observations in a small book by Dr Ord *On the influence of colloids upon crystalline form and cohesion*.

<sup>3</sup> *Phil. Trans.* for 1855. 179; and *C. S. Journal*, 9. 54.

196. Harcourt and Esson<sup>1</sup> examined two chemical processes, viz.



Their experiments shewed that the amount of the first change varied directly with the quantity of iodide present, other conditions remaining constant. If the quantity of  $\text{H}_2\text{SO}_4$  was made relatively large, then the amount of change varied with (1) the quantity of iodide, (2) the quantity of dioxide, (3) the time, (4) the total volume of the reacting substances, and (5) with 'some function of each of 'the other conditions under which the change occurs.' Among these other conditions, the influence of varying the quantities of acid, and of varying the temperature, were examined. It was found that the change was accelerated in proportion to the increase of the quantity of  $\text{H}_2\text{SO}_4$ . Other acids were tried, and the conclusion was arrived at that each acid has a definite 'acceleration-coefficient.'

The reactions between permanganic acid and oxalic acid in presence of sulphuric acid were found to be very complex; it appeared to be possible to analyse the change into four principal parts occurring simultaneously, and the results obtained pointed to the conclusion that for each part of the total operation the statement held good that 'when any 'substance is undergoing a chemical change of which no condition varies excepting the diminution of the changing substance, the amount of change occurring at any moment is 'directly proportional to the quantity of the substance.'

197. Menschutkin has studied the *velocities* and *limits* of the typical change which occurs when an alcohol and a carbon acid react to produce an ethereal salt and water<sup>2</sup>.

Certain fairly definite connections between the molecular weights and the structure of the acids and alcohols on the one hand, and the reaction-values of the change studied, on

<sup>1</sup> *Proc. R. S.* 14. 470 : 15. 262; and *C. S. Journal*, (2) 5. 460.

<sup>2</sup> For references, details of the methods, and of the plan adopted for stating the results, see book 1. chap. IV. par. 157.

the other hand, have been established by Menshutkin. Thus, by determining the velocity and limit of etherification of the various acids of the acetic series in the reactions between these acids and isobutylic alcohol, it is shewn that replacement of H in the  $C_nH_{2n+1}$  group of these acids is accompanied by an increase of the limit with a decrease of the velocity. These changes in the etherification-values are more marked when secondary acids are employed, and they reach their greatest values when tertiary acetic acids react on isobutylic alcohol.

When the acid is unchanged but the alcohol is varied, the velocity of etherification up to the point whereat equilibrium is established, increases by a constant amount for each increase of  $CH_2$  in the molecular weight of the alcohol used, provided the latter always belongs to the class of normal alcohols.

198. Kajander's<sup>1</sup> experiments on the rate of evolution of hydrogen by the action of various acids on thin plates of magnesium shew that the rate of this change varies with the temperature, the concentration and the nature of the acid employed.

199. But in all these cases the reaction chosen for examination was so complicated that no generally applicable conclusions could be deduced. If conclusions as to the equilibrium of chemical systems are to be deduced from observations of the velocities of changes undergone by these systems, then the simplest changes must be chosen, and, if possible, such as are unmixed with subsidiary physical operations.

One general conclusion appears fairly deducible from the experiments of those chemists whose work has been referred to in this section, namely, that each chemical substance which forms a member of any changing system exerts a specific action on the course of the changes which that system undergoes<sup>2</sup>.

<sup>1</sup> Abstracts in *Ber.* 14. 2053 and 2676 (original papers are in Russian).

<sup>2</sup> See *post*, chap. III. pars. 223 and 227. The more important memoirs, besides those already referred to, on the subject of this chapter are as follows: BER-

## CHAPTER III.

### AFFINITY.

#### *Introductory.*

200. FROM the beginning of the eighteenth, until the early years of the present century, chemists busied themselves with constructing *tables of affinity*. The conception which found expression in these tables was of the same kind as underlies such terms as relationship, kinship, &c. As there are degrees of relatedness, so, it was said, there are degrees of affinity. The same substance exhibits different degrees of affinity according to the nature of the other substances with which it reacts. When potash is heated with salammoniac, ammonia is produced, but when sand or silica is heated with the same salt there is no change; this, said Glauber, is because the potash 'loves and is loved by' the acid in the salammoniac.

Geoffrey, in 1718, drew up tables of affinity of which the following is a specimen.

ACIDS IN GENERAL	SULPHURIC ACID.	NITRIC ACID.
<i>fixed alkali,</i> <i>volatile alkali,</i> <i>absorbent earth,</i> <i>metals.</i>	<i>oily principle (phlogiston),</i> <i>fixed alkali,</i> <i>volatile alkali,</i> <i>absorbent earth,</i> <i>iron,</i> <i>copper,</i> <i>silver.</i>	<i>iron,</i> <i>copper,</i> <i>lead,</i> <i>mercury,</i> <i>silver.</i>

TROLLET, *Statique Chimique* 1. 409 *et seq.* WILLIAMSON, *Proc. R. S.* 16. 72. HURTER, *Chem. News* 22. 193. VAN'T HOFF, *Ber.* 10. 669; see also his *Études de Dynamique Chimique* (1884). POTILITZIN, *Ber.* 12. 2370. LEMOINE, *Ann. Chim. Phys.* (5) 12. 145. HOOD, *Phil. Mag.* (5) 6. 371 : 8. 121 : 13. 419. BERTHELOT, *Essai de Méc. Chimique* 2. 13, 58, 92, &c. HELL and URECH, *Ber.* 18. 531. The researches of Guldberg and Waage and of Ostwald are considered in detail in chap. III.

Each substance was said to have a greater affinity than those which came after it for the compound at the head of the column. Thus a compound of sulphuric acid and copper would be decomposed by the action of iron, or of any other substance placed above copper in the column headed sulphuric acid.

But it was gradually found that more than a single table was required for each substance, because the affinity of any substance for any other was not the same at all temperatures, and it also varied according as the reacting substances were solids or in solution. In 1775 Bergmann constructed tables of affinity for 59 substances, two for each, one representing the affinities at low temperatures when the substances reacted in solutions, and the other the affinities between the solid substances at high temperatures. Bergmann's table for potash, for instance, was constructed thus ;

## POTASH.

Wet way.		Dry way.	
<i>Sulphuric acid</i>		<i>Phosphoric acid</i>	
<i>Nitric</i>	"	<i>Boric</i>	"
<i>Hydrochloric</i>	"	<i>Arsenic</i>	"
<i>Phosphoric</i>	"	<i>Sulphuric</i>	"
<i>Arsenic</i>	"	<i>Nitric</i>	"
<i>Acetic</i>	"	<i>Hydrochloric</i>	"
&c. &c.		&c. &c.	

Bergmann also fully recognised that each constituent of any reacting substances exhibits affinity for each constituent of the other substances. This point was more fully insisted on in the tables of Guyton de Morveau (1786), of which the following is an example.

	SULPHURIC ACID.	NITRIC ACID.	HYDROCHLORIC ACID.	ACETIC ACID.
<i>Baryta</i>	66	62	36	29
<i>Potash</i>	62	58	32	26
<i>Soda</i>	58	50	28	25
<i>Lime</i>	54	44	20	19
<i>Ammonia</i>	46	38	14	20
<i>Magnesia</i>	50	40	16	17
<i>Alumina</i>	40	36	10	15

These numbers were not given as truly measuring affinities; but, it was said that the sum of the affinities of the products of a reaction is always greater than the sum of the affinities of the original substances. Thus, barium acetate is decomposed by potassium sulphate with the production of barium sulphate and potassium acetate. Now the affinity of baryta for acetic acid is represented in the table by the number 29, and that of potash for sulphuric acid by 62: but the numbers representing the affinities of barium for sulphuric acid and potash for acetic acid are 66 and 26 respectively; hence  $29 + 62 = 91$ , but  $66 + 26 = 92$ .

Bergmann regarded the relative quantities of acids needed to neutralise a given quantity of base (or *vice versa*) as measures of the affinities of the acids for that base. Thus he said that 100 parts by weight of potash are neutralised by  $78\frac{1}{2}$  parts of sulphuric acid, and by 64 parts of nitric acid; he therefore concluded that the affinity for potash of sulphuric acid is greater than that of nitric acid.

The phenomena of affinity were regarded by Boyle as connected with the mutual attractions between the small particles of bodies. Newton had adopted a similar view and had more especially insisted on the two-sidedness of this attraction<sup>1</sup>.

201. The subject of affinity was regarded by Berthollet (in the *Essai de Statique Chimique*) also from this point of view. The mutual attractions between the small particles of bodies which give rise to chemical phenomena Berthollet regarded as probably of the same kind as the mutual attractions which occur between the masses of bodies. The immediate effect of the affinity exerted by one substance on another is the combination of these substances. 'Every substance,' said Berthollet, 'which tends to enter into combination reacts by reason of its affinity and its mass'<sup>2</sup>.

But chemical action does not depend solely on affinity and mass. The physical states of the bodies, the degree of condensation or dilatation, &c. condition the chemical change;

<sup>1</sup> For a full historical account of affinity see Kopp's *Geschichte der Chemie* 2. 285—324.

<sup>2</sup> *Essai* 1. 2.



'these are the conditions which, in modifying the properties 'of the elementary parts of a substance, form what I call its 'constitution'<sup>1</sup>.

Berthollet thus distinguishes between chemical properties which do, and physical properties which do not, depend immediately on affinity. But at the same time he recognises the close connection between these properties; he even speaks of different kinds of affinity of which chemical affinity is one. As we saw in chapter II. (par. 173), Berthollet insists on the reciprocity of all chemical actions; even in the case of a liquid he regards the small particles as exerting mutual attraction, or, as he says, mutual affinity.

The object of Berthollet's *Essai* is to consider the causes which produce variations in the results of chemical action, i.e. the product of affinity and mass.

It should, I think, be especially noted that Berthollet recognised the possibility of reversing a chemical change by varying the conditions, more especially the masses of the reacting substances, under which the change proceeds. A substance with a small affinity for another, if present in large quantity, might decompose a compound of the second substance with another for which the affinity of the second substance was comparatively large. 'The measure of the affinity 'proper to every substance is', according to Berthollet's view, 'the saturation which it is able to produce with those substances that can combine with it'. It follows therefore that, that acid the smallest quantity of which is needed to saturate a given weight of a base has the greatest affinity for that base. We must remember that Berthollet<sup>2</sup> regarded chemical compounds as of no definitely fixed composition, and that he therefore had not gained the conception of equivalent, or combining, weights. We shall then see that his statement, that chemical action is proportional to the products of the masses and the affinities of the acting substances, really supplies a means for determining the equivalents of the reacting substances. Until Berthollet's theory of affinity was

<sup>1</sup> *Essai* 1. 3. See also *ante*, chapter II. par. 173.

<sup>2</sup> *Essai* 1. 535.

supplemented by the knowledge of the equivalent weights of acids, bases, and other compounds, it was of necessity unproductive.

The theories of affinity which prevailed before Berthollet were all founded on the assumption, that, if a substance,  $A$ , decomposes another,  $BC$ , with production of  $AC$  and  $B$ , then the affinity of  $A$  for  $C$  is greater than the affinity of  $B$  for  $C$ . Berthollet declared this conclusion to be erroneous. Whether  $A$  shall or shall not decompose  $BC$ , depends, according to Berthollet, not only on the affinities of  $A$  and  $B$  for  $C$ , but also on the quantities of  $A$  and  $BC$  which take part in the reaction.

202. When we come to more recent times, it is very difficult to gain a clear conception of the meaning of the term affinity<sup>1</sup>.

I think we shall do well to regard the subject, in the first place, from the dynamical point of view, as far as possible apart from any theory of the structure of matter.

The compounds,  $AB$  and  $CD$ , react to produce two new compounds,  $AC$  and  $BD$ ; there is mutual action and reaction. Looking at the transaction from one side only, we may say that  $AB$  exerts force on  $CD$ , or  $CD$  on  $AB$ . Now this force may be measured; (1) by finding the acceleration imparted to the acting masses of  $AB$  or  $CD$ , i.e. practically, by measuring the velocity of the chemical change; or (2) by arranging the conditions so that the new compounds,  $AC$  and  $BD$ , are free to act and react, in which case  $AC$  will exert force on  $BD$ , and  $BD$  on  $AC$ , the final result being the establishment of equilibrium in the whole system. By determining the masses of  $AB$ ,  $CD$ ,  $AC$ , and  $BD$ , present when this equilibrium is established we shall have the data for finding the ratio of the force tending to change  $AB$  and  $CD$  into  $AC$  and  $BD$ , to the force tending to change  $AC$  and  $BD$  back into  $AB$  and  $CD$ <sup>2</sup>.

<sup>1</sup> See, for instance, the article 'Affinity' in Watts's *Dictionary*, vol. 1.

<sup>2</sup> The dynamical expressions *force*, *velocity*, &c., are used here and throughout the paragraphs dealing with affinity in senses not strictly accurate, and which vary somewhat from time to time. This is especially marked in some of the quotations

But the question of affinity may be approached from another point. When actions and reactions between the parts of a material system are attended with changes in the configuration of the system, these actions and reactions are also attended with changes in the form and the distribution of the energy of the system. Hence, measurements of the losses or gains of energy of a chemical system under defined conditions may furnish data from which comparative estimates may be deduced of the mutual actions between members of that system. Measurements of the quantities of heat evolved or absorbed during definite chemical changes appear to afford the easiest means of measuring gains or losses of energy, and in this way of the comparative magnitudes of the affinities of different substances.

But before we can hope to gain exact measurements of affinity, we must have a clear conception of what it is we want to measure. Affinity, I think, is usually regarded as an action, or sometimes as the cause of an action, of some kind, which occurs between the atoms of chemical elements, such action resulting in a loss, or gain, of energy to the system of which these atoms are the constituents. Now it is possible that chemical affinity may be analogous to electrical potential; that as the existence of a difference of electrical potential between two particles implies the possibility of electrical work being done, so the existence of what might perhaps be called chemical potential between two atoms means the possibility of chemical work being done. If this supposition were adopted, we should look to electrical methods for the means of investigating chemical affinity.

To sum up. We may regard affinity as essentially connected with interatomic, and perhaps intermolecular, actions; and we may attempt to obtain measurements of different affinities by electrical methods: or we may be content to connect the term affinity with the actions and reactions which

from the memoirs of Guldberg and Waage. But it is almost impossible to do otherwise, unless one were to invent a series of new terms. To do this would, I think, be less advisable than to employ the terms in common use even if the meanings attached to them are less precise than could be wished.

occur when two, or more, chemically distinct substances combine to form new substances; and we may seek to deduce measurements of these actions, either from the velocities of the chemical changes, or from the conditions of equilibrium of the changing systems, or from observations of the changes of the energies of the reacting bodies.

The more important attempts which have been made to solve the problems of affinity may all, I think, be classed under these headings. Most important work has been done by Guldberg and Waage, and by Ostwald, in framing and applying a theory of affinity founded on measurements of the velocities of chemical changes, and of the conditions under which equilibrium is attained by given systems.

Berthelot and Thomsen have devoted themselves chiefly to the thermal aspects of the subject. Helmholtz, following on the older work of Berzelius, Faraday, Joule, and Thomson, has recently made some advances in applying electrical methods to these questions.

### SECTION I. *The Theory of Guldberg and Waage.*

203. We have seen how much Berthollet insisted on the importance of considering the relative masses of the reacting substances which take part in every chemical change. It is to this special part of the general question of affinity that Guldberg and Waage have chiefly devoted themselves<sup>1</sup>.

Berthollet's statement "Toute substance qui tend à entrer en combinaison agit en raison de son affinité et de sa 'quantité' (*Essai* 1. 2), has been extended and rendered more exact by the researches of these naturalists. They thus express themselves: "Suppose that two bodies, *A* and *B*, can be converted, by double decomposition, into *A'* and *B'*, and that *A'* and *B'* can be reconverted, under similar conditions, into *A* and *B*; neither of these changes will be complete. At the close of the reaction there will always be present four bodies, *A*, *B*, *A'* and *B'*; and the force which

<sup>1</sup> *Études sur les Affinités Chimiques* (Christiania, 1867), and *Journal für prakt. Chemie* (2) 19. 69.

'brought about the formation of  $A'$  and  $B'$  will be held in 'equilibrium by the force which caused the formation of ' $A$  and  $B$ . The force which caused the formation of  $A'$  and ' $B'$  increases in proportion to the *coefficient of affinity* of the 'reaction  $A + B = A' + B'$ , but it is also dependent on the 'quantities of  $A$  and  $B$ . We have found that *this force is 'proportional to the product of the active masses of  $A$  and  $B$ .* 'Representing the active masses of  $A$  and  $B$  by  $p$  and  $q$  'respectively, and the coefficient of affinity by  $k$ , we have the 'force  $= k.p.q$ ..... If the active masses of  $A'$  and  $B'$  be ' $p'$  and  $q'$  respectively, and the coefficient of affinity of the 'reaction  $A' + B' = A + B$  be  $k'$ , then the force which tends to 'bring about the re-formation of  $A$  and  $B$  is equal to  $k'.p'.q'$ . 'As this force is held in equilibrium by the other, we get the 'equation of equilibrium

$$k.p.q = k'.p'.q'.$$

'By experimentally determining  $p$ ,  $q$ ,  $p'$  and  $q'$ , the ratio ' $k:k'$  can be calculated; on the other hand, if this ratio has 'been determined, it is possible to calculate the result of the 'reaction for any initial condition of the four substances. If ' $P$ ,  $Q$ ,  $P'$  and  $Q'$  represent the number of molecules<sup>1</sup> of ' $A$ ,  $B$ ,  $A'$  and  $B'$  present before the action begins, and if  $x$  'represents the number of molecules of  $A$  and  $B$  transformed 'into  $A'$  and  $B'$ , and if we suppose that the total volume 'remains constant during the reaction, and is equal to  $V$ , 'then

$$p = \frac{P-x}{V}, q = \frac{Q-x}{V}, p' = \frac{P'+x}{V}, q' = \frac{Q'+x}{V}.$$

'Substituting these values for  $p$ , &c. in the equation of equi-  
'librium, and multiplying by  $V^2$ , we get

$$(P-x)(Q-x) = \frac{k'}{k}(P'+x)(Q'+x).$$

'The value of  $x$  is easily found by the help of this equa-  
tion<sup>2</sup>."

<sup>1</sup> In the original the expression is *les quantités absolues*; but it is evident from other parts of the memoir (e.g. p. 54) that this means the number of molecules.

<sup>2</sup> *Études*, pp. 6, 7.

The active mass of a substance is defined as the quantity of that substance in unit volume of the chemical system which undergoes change; all the substances being present in the ratios of their equivalent weights. The symbols  $p$  and  $q$  therefore represent certain numbers of equivalents of  $A$  and  $B$ .

The value of the coefficient of affinity of a reaction depends upon the nature of the reacting substances and on the temperature.

Inasmuch as the ratio  $k/k'$  is determined by a method of equilibrium, the chemical changes selected must be such as are composed of two equal and opposite actions. Such a change is that which occurs when alcohol and acetic acid react to produce ethylic acetate and water; after a time the action stops, and the system, alcohol, acetic acid, ethylic acetate, and water, remains in equilibrium. Moreover as the theory regards only the forces which are concerned in the production of the new compounds, and the re-formation of the original compounds, the reactions, from a study of which the value of  $k/k'$  is to be deduced, must be as simple as possible, in other words they must be as free as possible from all secondary actions. There should be one definite chemical change, and one only.

204. That we may have a clear conception of the meaning given by Guldberg and Waage to the expression *coefficient of affinity*, let us hear what they themselves say.

"In a simple decomposition of the form  $AB + C = AC + B$ , 'the formation of  $AC$  is chiefly brought about by the attraction between  $A$  and  $C$ ; but there are also attractions between 'the other substances, and the *force* which causes the formation of  $AC$  is the *resultant* of all these attractions. This 'force may be regarded as constant for a definite temperature; we represent its amount by  $k$ , which we call the '*coefficient of affinity* for the reaction in question. In the 'same way, in the double decomposition,  $AB + CD = AC + BD$ , 'the *force* which causes the formation of the new substances 'is a function of all the attractions between the bodies  $A, B,$

' $C, D, AB, CD, AC$ , and  $BD$ , and the *resultant force*,  $k$ , is the '*coefficient of affinity* for the reaction<sup>1</sup>."

"When the coefficient [of affinity] is equal to zero, or is 'negative, *no action* can proceed, but it must not be concluded 'that when no action occurs, the coefficient of affinity is equal 'to zero.... There are other causes which tend to stop the 'reaction. Besides  $A$  and  $B$ , there may be other bodies in 'the sphere of action,  $X, Y, Z$ , &c.; these we call *foreign 'bodies* (*les corps étrangers*). Between these and  $A$  and  $B$ , 'and also between these themselves, there are *chemical at- 'tractions*, which manifest themselves as forces tending to 'accelerate or retard the action between  $A$  and  $B$ . These 'attractions are of the same nature as the true *forces of 'affinity*; probably they follow the same laws. We suppose 'that the force produced in the action between  $A$  and  $X$ , and 'affecting the reaction between  $A$  and  $B$ , is proportional to the 'product of the active masses of  $A$  and  $X$ , and a coefficient,  $a$ , 'called by us the *coefficient of action*. In the same way may 'be represented the action between each of the other bodies, 'as regards  $A$  and  $B$ . Finally the mutual actions between 'the foreign bodies must be regarded. The attraction be- 'tween  $X$  and  $Y$  will produce a force, represented as  $aXY$ , 'which tends to accelerate or retard the action between  $A$  'and  $B$ . The same holds good for  $X$  and  $Z$ , &c. The *total 'force* causing the action between  $A$  and  $B$  is the resultant of 'all these actions, and is equal to the sum of all the forces 'we have to determine. Representing the active masses of '  $A, B, X, Y, Z$ ..... by  $p, q, X, Y, Z$ ,..... the *total force*,  $T$ , is 'expressed by the equation

$$T = kpq + apX + bqX + cXY + \dots$$

'The coefficients of action,  $a, b, c$ ,..... depend on the nature 'of the substances and the chemical reaction..... When the 'coefficient of action is positive, the force to which it corre- 'sponds tends to accelerate the chemical reaction, and when 'the coefficient is negative, the force tends to retard the re- 'action..... As a rule the coefficients of action are small

<sup>1</sup> *Études*, p. 6.

'compared with the coefficients of affinity, and as a consequence the total force is usually positive, and the substances  $A$  and  $B$  undergo change into  $A'$  and  $B'$ ."

205. Assuming that a chemical change proceeds during a sensible time, which varies for each change, it is possible to determine the affinity-coefficients from measurements of the velocity of the change. An attempt is made (*Études*, pp. 10, 11) to develop the necessary formulæ from the equations

$$v = \phi T, \text{ and } v = \phi (T - T'),$$

where  $v$  = the velocity of the change (i.e. the quantity of  $A' + B'$  produced from  $A + B$  in unit time), and  $\phi$  is a factor called by Guldberg and Waage the *coefficient of velocity*;  $T$  being the total force when  $A'$  and  $B'$  do not react to reproduce  $A$  and  $B$ ; and  $T'$  being the total force tending to reproduce  $A$  and  $B$  in those cases where  $A'$  and  $B'$  do react on each other.

206. There are two general methods by which the theory may be tested; in both cases it is necessary to arrange the experimental conditions so that the *forces of action* may be reduced as nearly as possible to zero.

I. Let there be four bodies  $A$ ,  $B$ ,  $A'$ , and  $B'$ , with the active masses  $p$ ,  $q$ ,  $p'$ , and  $q'$ ; let the coefficient of affinity for the reaction  $A + B = A' + B'$  be  $k$ , that for the reaction  $A' + B' = A + B$  be  $k'$ , and let the coefficients of action for  $A$  and  $A'$ ,  $A$  and  $B$ ,  $B$  and  $A'$ ,  $B$  and  $B'$ , be  $a$ ,  $b$ ,  $c$ , and  $d$ , respectively, and the coefficients of action for  $A'$  and  $A$ ,  $B'$  and  $A$ ,  $A'$  and  $B$ ,  $B'$  and  $B$ , be  $a'$ ,  $b'$ ,  $c'$ , and  $d'$ , respectively, then the total force for the reaction between  $A$  and  $B$  is

$$T = k p q + a p p' + b p q' + c q p' + d q q'.$$

And the total force for the reaction between  $A'$  and  $B'$  is

$$T' = k' p' q' + a' p' p + b' q' p + c' p' q + d' q' q.$$

When equilibrium is established  $T = T'$ ; then putting

$$a' - a = \alpha, \quad b' - b = \beta, \quad c' - c = \gamma, \quad d' - d = \delta,$$

<sup>1</sup> *Études*, pp. 8, 9. On p. 9 it is shewn that an equation of equilibrium can be obtained in which all the coefficients of affinity and the coefficients of action are represented. See next page.



the equation of equilibrium becomes

$$k p q = k' p' q' + \alpha p p' + \beta p q' + \gamma p' q + \delta q q'.$$

Then treating this equation in the same way as the more simple equation  $k p q = k' p' q'$  was treated on p. 408, an expression is obtained<sup>1</sup> by the use of which the amounts of *A* and *B* transformed into *A'* and *B'* when equilibrium is reached may be calculated for any initial system of the four bodies *A*, *B*, *A'* and *B'*.

This equation is applied (*Études*, pp. 53—55) to the system, acetic acid, alcohol, ethylic acetate, and water. The following numbers shew the close agreement between the observed and the calculated values of  $\xi$ , i.e. the quantities of alcohol and acid transformed into ethylic acetate and water when equilibrium is established.

#### VALUES OF $\xi$ .

SERIES I.	<i>Q</i>	Observed.	Calculated.
One molecule acid +	1	0.665	0.668
<i>Q</i> molecules alcohol.	1.5	0.779	0.772
	2	0.828	0.827
	2.8	0.856	0.870
	3	0.882	0.878
	12	0.932	0.930
	500	1.000	1.000
SERIES II.	<i>P</i>		
One molecule alcohol +	1	0.665	0.668
<i>P</i> molecules acid.	2	0.858	0.856
	5	0.966	0.972

<sup>1</sup> Let *P*, *Q*, *P'*, and *Q'* represent the numbers of molecules of *A*, *B*, *A'*, and *B'*, respectively, before the reaction begins, and let  $\xi$  represent the limit, or the quantities of *A* and *B* transformed into *A'* and *B'*, then the active masses of the four substances are given by the equations

$$p = \frac{P - \xi}{v}, \quad q = \frac{Q - \xi}{v}, \quad p' = \frac{P' + \xi}{v}, \quad q' = \frac{Q' + \xi}{v},$$

where *v* = total volume. Substituting these values in the equation of equilibrium given in the text, and multiplying by *v*<sup>2</sup>, the expression referred to in the text is obtained, viz.

$$k(P - \xi)(Q - \xi) = k'(P' + \xi)(Q' + \xi) + \alpha(P - \xi)(P' + \xi) + \beta(P - \xi)(Q' + \xi) + \gamma(P' + \xi)(Q - \xi) + \delta(Q - \xi)(Q' + \xi).$$

SERIES III.	$P'$	Observed.	Calculated.
One mol. acid +	0	0.665	0.668
one mol. alcohol +	0.13	0.626	0.648
$P'$ mols. ethyl acetate.	0.85	0.563	0.550
	1.6	0.521	0.487
SERIES IV.	$Q'$		
One mol. acid +	0	0.882	0.878
three mols. alcohol +	1	0.809	0.803
$Q'$ mols. water.	2	0.739	0.744
	8	0.468	0.512

If  $A$  and  $A'$  are solid bodies, while  $B$  and  $B'$  are liquids, then the active masses of  $A$  and  $A'$  remain practically constant throughout the reaction; if these masses are made equal, then the equation given on p. 408 for finding  $x$  becomes

$$Q - x = \frac{k'}{k} (Q + x)$$

and

$$x = \frac{Q - \frac{k'}{k} Q}{1 + \frac{k'}{k}}.$$

When the coefficients of action are taken into account, a modified form of this equation is easily obtained, viz.

$$Q - \xi = \frac{\lambda(Q + \xi) + \mu}{1 - \nu(Q - \xi)}$$

when  $\lambda$ ,  $\mu$  and  $\nu$  are constants<sup>1</sup>. From this the values of  $\xi$  can be determined by interpolation.

As examples of the application of the equation of equilibrium to systems containing solids we may take a few numbers from the tables on pp. 59 and 60. The action studied is that of the alkaline carbonates on barium sulphate;  $A$  = barium sulphate,  $B$  = alkaline carbonate,  $A'$  = barium carbonate,  $B'$  = alkaline sulphate.

#### VALUES OF $\xi$ .

SERIES I.	$Q$	Observed.	Calculated.
1 mol. barium sulphate +	3.5	0.719	0.715
500 mols. water (at 100°) +	2.5	0.500	0.500
$Q$ mols. potassium carbonate.	2	0.395	0.391
	1	0.176	0.178

<sup>1</sup> *Études*, p. 59.

SERIES II.	$Q$	$Q'$	Observed.	Calculated.
1 mol. barium sulphate +	2	0.25	0.200	0.198
500 mols. water (at 100°) +	3	0.25	0.408	0.409
$Q$ mols. potassium carbonate +	2	0.50	0. trace	0.000
$Q'$ mols. potassium sulphate.				

II. The theory may also be tested by calculating the quantities of the new substances  $A'$  and  $B'$  produced from  $A$  and  $B$  in a given time, by the help of formulæ obtained by developing the two equations already given as expressing the velocity of a reaction, viz.  $v = \phi T$ ; and  $v = \phi(T - T')$ . This is done for the system alcohol + acetic acid, &c., and for the system barium sulphate + alkaline carbonate, &c. (*Études*, pp. 55—58; and 60—61). The formulæ are complicated; the observed results agree very well with the calculated numbers<sup>1</sup>.

207. Having established their theory by the experiments and calculations detailed in their first memoir, Guldberg and Waage proceed to apply it to various classes of chemical reactions<sup>2</sup>. Formulæ, obtained from the two fundamental equations

$$(1) k \cdot p \cdot q = k' \cdot p' \cdot q' \quad \text{and} \quad (2) v = \phi(T - T''),$$

are applied to calculate the amount of change when equilibrium is established in systems consisting of (a) four soluble substances, (b) two soluble and two insoluble substances, (c) an indefinite number of soluble substances, (d) gaseous substances arising from the dissociation of a solid, and (e) gaseous substances only<sup>3</sup>.

208. In applying the theory to systems containing gaseous constituents, and more especially to systems undergoing dissociation, it is almost necessary that some hypothesis should be adopted regarding the mechanism of chemical change. The hypothesis adopted by Guldberg and Waage is essentially the same form of the molecular and atomic theory as has been applied by Pfaundler to the subject of chemical

<sup>1</sup> But see *post*, par. 221.

<sup>2</sup> *Journal für prakt. Chemie* (2) 19. 69.

<sup>3</sup> For details see the original paper, *loc. cit.*, or the condensed translation in *Phil. Mag.* (5) 8. 181.

equilibrium in general<sup>1</sup>. In an apparently homogeneous molecular system there must always be many molecules in a condition more or less divergent from the mean state of the system. Let the molecules of two substances which act chemically on one another be represented by  $A$  and  $B$ ; let these molecules be composed of the atoms (or atomic groups)  $aa$ , and  $bb$ , respectively, performing certain vibrations within the molecules  $A$  and  $B$ . At certain points in these vibrations the force between  $a$  and  $a$ , and between  $b$  and  $b$  will be at a minimum; if at this moment  $A$  and  $B$  approach each other, chemical action will occur with the production of new molecules,  $C$ , composed of the atoms  $ab$ . If the number of molecules of  $A$  which are in this condition of readiness to undergo change be  $\alpha'$ , the total number of molecules of  $A$  in unit volume of the system being  $\alpha$ , and if the number of molecules of  $B$  ready to undergo change be  $\beta'$ , the total number of molecules of  $B$  being  $\beta$ , then the velocity of formation of the new molecules,  $C$ , may be represented by the equation  $\phi \cdot \alpha \alpha' \beta \beta' = k \alpha \beta$ , when  $k = \phi \alpha' \beta'$ . The factor  $\phi$  depends on the temperature, and the chemical nature of the substances  $A$  and  $B$ ; the nature of this dependence must be experimentally determined. An expression, similar to that given, can be found for the velocity of re-formation of  $A$  and  $B$ ; and hence the amounts of  $A$ ,  $B$ , and  $C$ , which are present when equilibrium is attained can be calculated for any initial state of the system.

209. The application of this method to cases of dissociation is considered in detail in Guldberg and Waage's second paper<sup>2</sup>, where formulæ are deduced, by the help of the considerations sketched in the preceding paragraph, for finding the equilibrium of a gas which dissociates into two or more constituents, along with which a definite amount of the original gas is also present. The formulæ are applied chiefly to the cases of nitrogen tetroxide, and hydriodic acid, which dissociate when heated into nitrogen dioxide ( $\text{NO}_2$ ), and hydrogen and iodine, respectively.

<sup>1</sup> See *ante*, chap. II. par. 187.

<sup>2</sup> *J. für prakt. Chemie* (2) 19. 102—114.

210. Guldberg and Waage have established the proposition, that, when secondary actions are eliminated, the amount of any chemical change is proportional to the products of the active masses of the substances concerned and the coefficients of affinity of the reaction. They have shewn that the values of the coefficients of affinity of various reactions can be determined in terms of the coefficient of one of the reactions taken as equal to unity; and they have made a few determinations of these values. But their object has been rather to establish a general theory than to carry out its application in one particular direction. Moreover the reactions studied by Guldberg and Waage are, for the most part, too complex for the purpose of finding data from which the values of different coefficients of affinity may be deduced, however admissible the reactions may be for testing the theory which these naturalists have proposed.

This theory has been applied to the determination of the relative coefficients of affinity of various changes by Ostwald.

211. It is necessary to eliminate as far as possible all secondary actions from the chemical changes chosen for study. When two substances react, in solution, to form two new substances, which also remain in solution, we have probably as simple a case as can be found for applying Guldberg and Waage's theory. But a difficulty arises. How is the amount of change to be experimentally determined? Let  $A$  and  $B$  react to produce  $A'$  and  $B'$ , all the substances being dissolved in water: if it is attempted to determine the quantities of  $A'$  and  $B'$  produced, by ordinary analytical methods, e.g. by precipitation as insoluble salts, the addition of the necessary reagents disturbs the equilibrium of the system, and thus produces changes in the quantities of  $A$ ,  $B$ ,  $A'$  and  $B'$  present, whereby any measurement of the coefficient of affinity is rendered untrustworthy. It would therefore appear that the amount of chemical action, in a case such as we are considering, must be determined by measuring the magnitude of some physical constant, or constants, of the system, before and after the chemical operation.

The application of physical measurements to the quantitative investigation of chemical changes seems to have been first made by Steinheil<sup>1</sup> in 1843. The thermal methods of Thomsen, the magnetic methods used by G. Wiedemann, the chromometric methods employed by A. Müller, and the volumetric and optical processes adopted by Ostwald, are all examples of the application of the same general conception<sup>2</sup>.

212. Ostwald has sought to find the *relative affinities* (see p. 418, also *post*, pars. 214-218, 223, 227, and 235) of various acids. The analytical method employed in his earliest paper was to measure the specific volumes<sup>3</sup> of aqueous solutions containing equivalent quantities of (1) acids, (2) bases, and (3) mixtures of acids and bases<sup>4</sup>.

In the reaction  $A + B = A' + B'$ , let  $A$  and  $A'$  be two acids, and  $B'$  and  $B$  their neutral salts with the same base,  $B'$  being the salt of acid  $A$ , and  $B$  the salt of acid  $A'$ . Then according to Guldberg and Waage's theory we have

$$k(P-x)(Q-x) = k'(P'+x)(Q'+x)^5.$$

From this, the ratio  $k'/k$  can be determined. If for the sake of simplicity  $k'$  is taken as equal to  $1/k$ , the equation becomes

$$k^2(P-x)(Q-x) = (P'+x)(Q'+x).$$

<sup>1</sup> *Annalen* 48. 153.

<sup>2</sup> The more important memoirs on this subject are these: K. HOFMANN, *Pogg. Ann.* 133. 575. THOMSEN, *Pogg. Ann.* 138. 65, and many other papers; see *Thermochemische Untersuchungen*, vol. I. KRECKE, *J. für prakt. Chemie* (2) 3. 286. BERTHELOT and SAINT-MARTIN, *Ann. Chim. Phys.* (4) 26. 433 (and other papers). A. MÜLLER, *Pogg. Ann. Ergänzbd.* 6. 123. G. WIEDEMANN, *J. für prakt. Chemie* (2) 9. 145. DIBBITS, *Pogg. Ann. Ergänzbd.* 7. 462. BOGUSKI and KAJANDER, *Ber.* 9. 1646. GLADSTONE, *Phil. Trans.* for 1855. 179. GLADSTONE and DALE, *Phil. Trans.* for 1863. 317. LANDOLT, *Pogg. Ann.* 123. 595. WÜLLNER, *Pogg. Ann.* 133. 1. RÜDORFF, *Ber.* 6. 482 and 643. OSTWALD, *J. für prakt. Chemie*, (2) 25. 1. WIEDEMANN, *Wied. Ann.* 17. 561. KRÜSS, *Ber.* 15. 1243; 16. 2051. RAOULT, *Compt. rend.* 94. 1517; 95. 1030; 97. 941; 98. 509, 1047. Also *Ann. Chim. Phys.* (3) 28. 133; (6) 2. 66.

<sup>3</sup> Specific volume = volume of unit weight referred to water (at 20°) as unity.

<sup>4</sup> Ostwald's papers are to be found in the *Journal für prakt. Chemie.* (2) 18. 385; 18. 328; 19. 468; 22. 251; 23. 209 and 517; 24. 486; 27. 1; 28. 449; 29. 385.

<sup>5</sup> See *ante*, par. 203.

When one acid reacts on the neutral salt of another, in equivalent quantities, then  $P = Q = 1$ ;  $P' = Q' = 0$ , and the equation has the form

$$k^2(1-x)^2 = x^2, \text{ or } k = \frac{x}{1-x};$$

where  $x$  = the amount of salt  $B$  decomposed, and  $(1-x)$  = the amount of salt  $B$  undecomposed, by the acid  $A$ ; or, as equivalent quantities are used,  $x$  = amount of base combined with acid  $A$ , and  $(1-x)$  = amount of base combined with acid  $A'$ . Hence, in the reactions of two acids on the neutral salt of one of the acids, the affinity-coefficients may be defined as the proportions in which the base is shared (*das Theilungsverhältniss der Basis*) between the two acids, when the three substances react in equivalent quantities. 'The amount of base combined with each acid is, however, a measure of the affinity of the acid for that base; the affinity-coefficients therefore express the ratios of these affinities, i.e. they express the *relative affinities* of the acids for the 'base'. The values of these relative affinities of acids must be determined for different bases and at different temperatures.

When aqueous solutions of equivalent quantities of acids and bases are mixed, the volume of the product is not equal to the sum of the volumes of the constituents. If the temperature and the concentration of the solutions are kept constant, the change of volume is found to depend upon the nature of the acid, and of the base. In Ostwald's experiments a solution of normal concentration was one containing one equivalent of acid, or base, in grams, in 1000 grams of solution. The temperature was 20° C.

Let the change of volume observed on mixing normal solutions of acid  $A$  with base  $C$  be represented by  $v$ , and the change when acid  $A'$  is mixed with the same base,  $C$ , by  $v'$ ; let both acids act simultaneously on the base, acid  $A$  combining with  $x$  parts, and acid  $A'$  with  $1-x$  parts of the base, then the volume-change in the last reaction,  $v_0$ , is made up

<sup>1</sup> Ostwald, *loc. cit.* 16. 386.

of two parts, viz. that attending the formation of  $x$  parts of the salt  $AC$ , and that attending the formation of  $(1-x)$  parts of the salt  $A'C$ , hence

$$v_0 = xv + (1-x)v', \quad \therefore x = \frac{v_0 - v'}{v - v'}.$$

The values of  $v$  and  $v'$ , and hence the difference  $v - v'$ , can generally be directly determined; but in many cases it is preferable to determine the difference  $v - v'$  by an indirect method.

The method is given by Thomsen<sup>1</sup>. If an equivalent of acid  $A'$  is added to the salt  $AC$ , and an equivalent of the acid  $A$  to the salt  $A'C$ , then the difference between the observed volume-changes is equal to the desired difference  $v - v'$ . The method is founded on the theorem, that, in homogeneous solutions containing equal quantities of the same constituents, the final arrangement of the constituents is the same whatever may have been the initial arrangement<sup>2</sup>.

Representing the observed change of volume when  $A$  acts on  $A'C$ , by  $v_1$  and the change when  $A'$  acts on  $AC$  by  $v_2$ , and putting  $\xi$  as equal to the sum of all the secondary reactions, the equation already given for finding  $x$  becomes

$$x = \frac{v_1 - \xi}{v_1 - v_2}; \quad \text{and} \quad 1 - x = -\frac{v_2 - \xi}{v_1 - v_2}.$$

213. As an example of the application of this method, let us glance at Ostwald's first attempt to determine the relative affinities of the acids  $H_2SO_4$ ,  $H_2Cl_2$ , and  $H_2N_2O_6$ , for the bases  $KOH$ ,  $NaOH$ ,  $NH_4OH$ ,  $MgO$ ,  $ZnO$ , and  $CuO$ . The normal solutions required were 21 in number; 3 for the acids, and 3 for each base, viz. solutions of the nitrate, chloride, and sulphate. The 'volume' of each solution, i.e. the volume which contained one *gram-molecule* of the acid or salt, was determined at  $20^\circ$ , and then the expansion of the liquid was found by experiment for the interval  $0^\circ$ — $60^\circ$ ; the 'volume' at any temperature between  $0^\circ$  and  $60^\circ$  could then be calculated. Besides determining the 'volumes' of the original solutions, and of the solutions obtained by mixing the

<sup>1</sup> *Pogg. Ann.* 138. 86.

<sup>2</sup> This is experimentally proved to be correct.



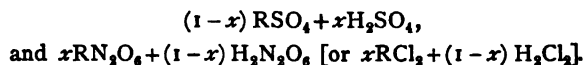
various acids and salts, it was necessary to measure the volume-change (if any) which occurred when a given acid was mixed with the solution of its own neutral salt, in order to find data for calculating the value of  $\xi$  in the equation to be afterwards employed. The results are tabulated as follows.

$v_1$ =volume-change attending the action of nitric acid, or hydrochloric acid, on sulphates ;

$v_2$ =volume-change attending the action of sulphuric acid on chlorides or nitrates.

Base.	Nitric against sulphuric acid.			Hydrochloric against sulphuric acid.		
	$v_1$ ;	$v_2$ ;	$v_1 - v_2$ ;	$v_1$ ;	$v_2$ ;	$v_1 - v_2$
Potash	+ 14'00	- 2'38	+ 16'38	+ 13'08	- 2'09	+ 15'17
Soda	+ 13'77	- 2'73	+ 16'50	+ 13'00	- 2'52	+ 15'52
Ammonia	+ 11'64	- 2'70	+ 14'34	+ 11'45	- 2'78	+ 14'23
Magnesia	+ 10'58	- 3'06	+ 13'64	+ 10'47	- 3'05	+ 13'52
Zinc oxide	+ 8'86	- 3'11	+ 11'97	+ 9'08	- 3'32	+ 12'40
Copper oxide	+ 7'85	- 3'42	+ 11'27	+ 8'06	- 3'49	+ 11'55.

The volume-changes attending secondary reactions were also measured and tabulated. The sum of these secondary reactions,  $\xi$ , is made up of the parts



The change of volume attending the last of these reactions was found to be equal to zero.

214. From these data the value of  $x$  is found for each base and pair of acids by the equation  $x = \frac{v_1 - \xi}{v_1 - v_2}$ ; and from these values the relative affinities of each pair of acids for each base are calculated. The relative affinities are those of (1)  $\frac{\text{H}_2\text{N}_2\text{O}_6}{\text{H}_2\text{SO}_4}$ , (2)  $\frac{\text{H}_2\text{Cl}_2}{\text{H}_2\text{SO}_4}$ , and (3)  $\frac{\text{H}_2\text{Cl}_2}{\text{H}_2\text{N}_2\text{O}_6}$ . The first and second are calculated by help of the equation  $k = \frac{x}{1-x}$ , and the third is obtained indirectly by dividing the second by the first, the value of the difference  $v_1 - v_2$  being too small in this case to allow of a trustworthy result being obtained by

direct calculation. The following table exhibits the relative affinities of the three pairs of acids.

## RELATIVE AFFINITIES.

<i>Base.</i>	I. $\frac{\text{H}_2\text{N}_2\text{O}_6}{\text{H}_2\text{SO}_4}$	II. $\frac{\text{H}_2\text{Cl}_2}{\text{H}_2\text{SO}_4}$	III. $\frac{\text{H}_2\text{Cl}_2}{\text{H}_2\text{N}_2\text{O}_6}$
Potash	$\frac{0.667}{0.333} = 2.00$	$\frac{0.659}{0.341} = 1.94$	$\frac{1.94}{2.00} = 0.97$
Soda	$\frac{0.667}{0.333} = 2.00$	$\frac{0.657}{0.343} = 1.92$	$\frac{1.92}{2.00} = 0.96$
Ammonia	$\frac{0.652}{0.348} = 1.88$	$\frac{0.644}{0.356} = 1.81$	$\frac{1.81}{1.88} = 0.96$
Magnesia	$\frac{0.638}{0.362} = 1.76$	$\frac{0.635}{0.365} = 1.74$	$\frac{1.74}{1.76} = 0.99$
Zinc oxide	$\frac{0.617}{0.383} = 1.61$	$\frac{0.605}{0.395} = 1.53$	$\frac{1.53}{1.61} = 0.95$
Copper oxide	$\frac{0.591}{0.409} = 1.44$	$\frac{0.584}{0.416} = 1.40$	$\frac{1.40}{1.44} = 0.97.$

215. The ratio of the affinities of hydrochloric and nitric acids is evidently independent of the nature of the base, whereas in the case of sulphuric and hydrochloric, or sulphuric and nitric acids, the ratio varies in accordance with the nature of the base. The reason for this apparent difference is to be sought for in the numbers which express the volume-changes attending the action of sulphuric acid on neutral sulphates. Ostwald shews that when sulphuric acid and neutral sulphates react in equivalent quantities, only a portion of the sulphate is changed into the acid salt, and that the amount of this change depends on the base present in the neutral sulphate. Hence, Ostwald concludes, that 'sulphuric acid...does not exert affinity on a base with its whole mass but only with that part which is not combined to form acid sulphate. The greater this part, the smaller will the affinity of sulphuric acid appear to be.' It is probable that the true relative affinity of sulphuric acid, like that of hydrochloric and nitric acids, is independent of the nature of the base with which the acid combines.

216. The influence of temperature on the relative affinities of the three pairs of acids is then examined by Ostwald in the same way as has been employed for examining the influence of the nature of the base.

The results are contained in the following table.

RELATIVE AFFINITIES (for Soda).

Temp.	I. $\frac{\text{H}_2\text{N}_2\text{O}_8}{\text{H}_2\text{SO}_4}$ .	II. $\frac{\text{H}_2\text{Cl}_2}{\text{H}_2\text{SO}_4}$ .	III. $\frac{\text{H}_2\text{Cl}_2}{\text{H}_2\text{N}_2\text{O}_8}$ .
0°	$\frac{0.655}{0.345} = 1.90$	$\frac{0.659}{0.341} = 1.93$	$\frac{1.93}{1.90} = 1.02$
20°	$\frac{0.667}{0.333} = 2.00$	$\frac{0.657}{0.343} = 1.92$	$\frac{1.92}{2.00} = 0.96$
40°	$\frac{0.669}{0.331} = 2.02$	$\frac{0.666}{0.334} = 1.99$	$\frac{1.99}{2.02} = 0.98$
60°	$\frac{0.703}{0.297} = 2.37$	$\frac{0.703}{0.297} = 2.37$	$\frac{2.37}{2.37} = 1.00$

Here again the relative affinities of hydrochloric and nitric acids remain constant, while that of sulphuric acid varies with variations of temperature. The variation in the value of the relative affinity of sulphuric acid is shewn to be inversely as the amount of combination of the acid with the neutral sulphate; this confirms the provisional conclusion that the true relative affinity of sulphuric acid is in all respects comparable with the relative affinities of hydrochloric and nitric acids.

The final result of the experiments detailed in Ostwald's first paper is, that, *the relative affinities of the acids are expressed by constant numbers.*

217. In his second paper<sup>1</sup>, Ostwald extends the volumetric method to a number of acids, both monobasic and dibasic, including several carbon-acids. He has also, in this paper, determined the refractive indices of many of the solutions of acids, bases, and salts already employed, and from these he has arrived at measurements of the amounts of change; so that most of the data on which his calculations are based

<sup>1</sup> *loc. cit.* 18. 328.

have been gained by two independent methods. The results agree very well; Ostwald, however, thinks that the volumetric method gives more trustworthy results than the optical method. The following table presents the results of the volumetric experiments, with monobasic acids, contained in Ostwald's second paper.

PROPORTIONS IN WHICH BASES ARE SHARED AMONG MONOBASIC  
ACIDS.

Acids.	Potash.	Soda.	Ammonia.	Mean.
1 Dichloracetic : nitric	77	77	75	76
2 Dichloracetic : hydrochloric	74	75	73	74
3 Dichloracetic : trichloracetic	70, 73	71, 71	70, 72	71
4 Dichloracetic : lactic	8	9	11	9
5 Monochloracetic : trichloracetic	92	92	92	92
6 Formic : trichloracetic	97	96	97	97
7 Formic : lactic	43	46	48	46
8 Formic : acetic	25	23	23	24
9 Formic : butyric	21	21	19	20
10 Formic : isobutyric	19	19	18	19
11 Butyric : acetic	54	52	53	53
12 Isobutyric : acetic	56	51	53	53
13 Propionic : formic	78	80	79	79
14 Glycollic : formic	43	44	45	44

One equivalent of the neutral salt (of potassium, sodium, or ammonium) of the acid placed first in column I. is acted on by one equivalent of the acid placed after it in the same column; the numbers in the columns of bases represent the percentage amounts of base withdrawn from the first acid by the action of the second.

218. Ostwald's former investigation shewed that the relative affinities of nitric and hydrochloric acid are nearly identical, the latter being rather smaller than the former<sup>1</sup>. If the relative affinity of nitric acid is taken as 100, that of hydrochloric acid is expressed by the number 98. The relative affinity of dichloracetic acid may be calculated in terms of either nitric or hydrochloric acid. Thus,

<sup>1</sup> This is confirmed by Thomsen's thermochemical work. *Pogg. Ann.* 138. 65.

$$(1) \text{ Nitric acid} = 100; \text{ dichloracetic acid} = \frac{24}{76} \times 100 = 32.$$

$$(2) \text{ Hydrochloric acid} = 98; \text{ dichloracetic acid} = \frac{26}{74} \times 98 = 34.$$

From this, the relative affinities of trichloracetic and lactic acids were found. Thus,

$$\text{Trichloracetic acid} = \frac{71}{29} \times 33 = 80.$$

$$\text{Lactic acid} = \frac{9}{91} \times 33 = 3.3.$$

Then taking trichloracetic acid as 80, we determine the relative affinities of monochloracetic and formic acids. Thus,

$$\text{Monochloracetic acid} = \frac{8}{92} \times 80 = 7.$$

$$\text{Formic acid} = \frac{3}{97} \times 80 = 2.5.$$

But if we start with lactic acid as 3.3, and calculate the relative affinity of formic acid, we get  $\frac{54}{46} \times 3.3 = 3.9$ , a number very much larger than that obtained from former data. Similarly, the numbers obtained for the relative affinities of butyric and isobutyric acids shew considerable differences.

The numbers obtained for the relative affinities of most of the acids examined by Ostwald in this research cannot be regarded as final; the method whereby these numbers are obtained is however shewn to be satisfactory; and the determination of the relative affinities of acids in terms of some one taken as unity is exhibited as a legitimate object of research.

219. In his later investigations Ostwald attempts to use chemical methods in attacking the problem of the relative affinities of acids.

When one substance in solution reacts on another in the solid state, so that there is always an excess of the latter present, the active mass of the solid remains constant<sup>1</sup>. The equation already given (par. 212) viz.

$$k^2 (P-x)(Q-x) = (P'+x)(Q+x)$$

becomes

$$k^2 (P-x)c = (P'+x)(Q+x),$$

<sup>1</sup> See Guldberg and Waage, *J. für prakt. Chemie* (2) 19. 88.

where  $c$  remains unchanged, as it expresses the constant active mass of the solid substance.

Suppose it is desired to find the relative affinity of an acid by this method; the acid is allowed to react on the insoluble salt of another acid, with the base of which salt the given acid forms a soluble compound. Let  $P$  represent the acid,  $Q$  the insoluble salt,  $P'$  the acid of this salt, and  $Q'$  the soluble salt produced in the reaction. At the beginning of the action  $P' = Q' = 0$ . The active mass of  $Q = c$ , and the only other independent variable,  $P$ , can be taken as equal to 1.

Then the equation given above becomes

$$k^2(1-x)c = x^2; \text{ hence } k = \frac{x}{\sqrt{c(1-x)}}.$$

If experiments are conducted with different acids and the same insoluble salt, various affinity-coefficients are obtained of the form

$$k_1 = \frac{x_1}{\sqrt{c(1-x_1)}}, \quad k_2 = \frac{x_2}{\sqrt{c(1-x_2)}}, \quad \&c.$$

Hence 
$$\frac{k_1}{k} = \frac{x_1}{x} \frac{\sqrt{1-x}}{\sqrt{1-x_1}}, \quad \frac{k_2}{k} = \frac{x_2}{x} \frac{\sqrt{1-x}}{\sqrt{1-x_2}}.$$

The unknown quantity  $c$  has disappeared, and the quotients  $\frac{k_1}{k}, \frac{k_2}{k} \dots$  represent the relative affinities of the different acids in terms of the first<sup>1</sup>.

220. The reactions actually studied by Ostwald were (1) that which occurs when an acid acts on solid zinc sulphide, producing sulphuretted hydrogen and a soluble zinc salt; and (2) the action of acids on solid calcium oxalate and zinc oxalate, whereby oxalic acid and a soluble calcium (or zinc) salt are formed.

The first reaction was however abandoned because of the impossibility of obtaining physically homogeneous zinc sulphide<sup>2</sup>.

The second reaction was found to be also open to objections. Small changes in the physical state of the oxalate

<sup>1</sup> Ostwald, *loc. cit.* (2) 19. 473—474.

<sup>2</sup> For details see Ostwald, *loc. cit.* (2) 19. 475—479.

used were accompanied by marked irregularities in the chemical change. What Ostwald calls the *stability* of the calcium (or zinc) oxalate conditions the quantity of this salt dissolved by an acid in a given time. The stability is itself dependent on the preparation of the salt, more especially on the amount of water it contains, and on the degree of dilution of the acid employed. Another circumstance tending to alter the stability is the presence, or absence, of the neutral alkaline (or magnesium) salt of the acid used in the reaction. Mono-basic acids exert a greater solvent action, in a given time, in presence of their neutral salts than when those salts are absent; the solvent action of polybasic acids, on the other hand, is diminished by the presence of their neutral salts. This subject is worked out in detail by Ostwald, and it is shewn that the neutral salt probably acts on the calcium (or zinc) oxalate to a very small extent and decomposes a little of it, and that the solvent action of the acid is increased by this change in the stability of the oxalate<sup>1</sup>. Developing this hypothesis, and applying the theory of Guldberg and Waage, Ostwald arrives at the result, that the modifying influence on the chemical equilibrium of a system, exerted by the *stability* of a solid member of that system, is of the same nature as the influence exerted by the *affinities* of the reacting substances<sup>2</sup>. As regards the modifying influence of dilution it is shewn that the amount of calcium (or zinc) oxalate dissolved increases, up to a certain limit, as the quantity of water present increases. The action of water is probably twofold; (1) it forms more or less stable compounds with the acid, and thus reduces the solvent action of the latter; (2) it exerts a decomposing action on the oxalate, and thus increases the solvent action of the acid. In the cases studied, the latter action preponderated<sup>3</sup>.

As a general result of this part of his research, Ostwald concludes, that the action of the acids on insoluble salts

<sup>1</sup> Ostwald, *loc. cit.* (2) 23. 218—222.

<sup>2</sup> Do. do. (2) 23. 222—226.

<sup>3</sup> Do. do. (2) 23. 527—528; and do. (2) 22. 305 *et seq.* See also *ante*, chap. II. par. 181.

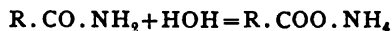
presents a suitable means for determining the relative affinities of these acids, provided the solutions of the acids employed are as dilute as possible<sup>1</sup>.

221. The methods thus far employed by Ostwald have been based on the study of the equilibrium of chemical systems wherein two equal and opposite processes of change are proceeding. But, as we saw in par. 205, the theory of Guldberg and Waage may also be applied to determine the values of coefficients of affinity from measurements of the velocities of chemical operations. Guldberg and Waage themselves tested their theory by applying it in this way. The chemical change, whose velocity is to be observed, must be a simple process, otherwise the difficulties of calculation become at present insurmountable, but it must also be a representative process, otherwise the results are not capable of wide application<sup>2</sup>.

Ostwald therefore determined to measure the velocities of some of those processes the relative affinities of the substances taking part in which had already been roughly determined by equilibrium-methods.

He would thus find values for these affinities by two different applications of the theory of Guldberg and Waage.

222. The operation formulated as



occurs in the presence of acids; the velocity of the change depends on the dilution of the acid employed, the temperature, and the nature of the acid which exerts a 'predisposing affinity' (see *ante*, chap. II. par. 179) on the reaction. The process proceeds evenly, and the velocity is easily determined by measuring the amount of ammonium salt produced, by decomposition with sodium hypobromite<sup>3</sup>.

<sup>1</sup> *loc. cit.* (2) 23. 536.

<sup>2</sup> The results obtained by Menshutkin, Kajander, and others, as also those detailed in Guldberg and Waage's *Études*, are not suitable for deducing the values of coefficients of affinity. (See Ostwald, *loc. cit.* (2) 27. 1.)

<sup>3</sup> Ostwald, *loc. cit.* (2) 27. 1. Many preliminary trials were made, and the value of a small correction for the nitrogen evolved by the amide present was determined: for a description of the methods of procedure see pp. 5—14.



Acetamide was employed; the experiments were made at 65° and 100°, for intervals of time varying from 2 minutes to 50 days.

The amounts of chemical change, for given intervals of time, at a constant temperature, are determined and tabulated for each acid employed; then, by the use of an interpolation-formula, the time is found which is required by each acid to accomplish 50 per cent. of the total change; and lastly, by dividing the intervals of time in the first table by the times required for the half-completion of the process, comparable numbers are obtained which express the amount of change effected by each acid in the same time. Putting the velocity as inversely proportional to the time required for reaching a determinate stage of the decomposition, it is shewn that the ratios of the velocities of different acids are not constant, but depend on the stage of the operation selected.

Ostwald, as we have seen, selects the stage at which the operation is half completed; the velocities are stated in terms of that of hydrochloric acid taken as 100.

#### RELATIVE VELOCITIES.

		65°	100°
Hydrochloric	acid	100	100
Nitric	"	98	97
Hydrobromic	"	98	98
Trichloracetic	"	80	—
Dichloracetic	"	40·8	—
Monochloracetic	"	13·0	—
Formic	"	5·1	4·83
Lactic	"	5·13	4·85
Acetic	"	2·34	—
Sulphuric	"	65·4	59·4
Oxalic	"	22·6	20·5
Tartaric	"	7·51	7·32
Malic	"	4·67	—
Succinic	"	2·55	2·5
Citric	"	4·01	4·01
Phosphoric	"	—	3·58
Arsenic	"	—	3·53

A curve theoretically representing the progress of the change is constructed by help of the formula  $\frac{y}{a-y} = Ct$ , where  $y$  = amount of acid decomposed in time  $t$ , the active mass of which acid at the beginning of the reaction is represented by  $a$ , and  $C$  = a constant.

This equation is obtained by developing the fundamental equation given by Guldberg and Waage<sup>1</sup>,  $v = \phi(T - T')$ ; it therefore assumes the correctness of the law of mass-action formulated by these naturalists, and also that the substances formed during the reaction exert no influence on the process. The actually observed results are plotted alongside the theoretical curve; the curves representing the process at 65° and 100° are nearly identical.

A comparison of the curve calculated by the formula, with the results plotted alongside, shews that the process is not entirely free from secondary reactions. Among these secondary reactions are to be placed the influence of the neutral ammonium salts of the monobasic acids (see *ante*, par. 220), the influence of the acid ammonium salts of the polybasic acids, and the probable formation of amido-acids in the case of trichloroacetic acid, &c. Nevertheless, the numbers obtained are comparable with those arrived at by Ostwald's former equilibrium-studies, inasmuch as the secondary changes in both series of reactions are very similar<sup>2</sup>.

223. In a former paper it had been shewn by Ostwald, that when equilibrium is established by the competition of two acids for the same base, the factors  $k$  and  $k'$  in Guldberg and Waage's fundamental equation, may with great probability be resolved each into two parts, one dependent on the nature of the base, and the other on the nature of the acids<sup>3</sup>. Treating  $k$  and  $k'$  in this way, he gets

$$k = c \frac{a \cdot \beta}{a' \cdot \beta}, \text{ and } k' = c \frac{a' \cdot \beta}{a \cdot \beta};$$

where  $a$  and  $a'$  depend on the nature of the acids, and  $\beta$  on

<sup>1</sup> For details see Ostwald, *loc. cit.* (2) 27. 24 and 31.

<sup>2</sup> For further discussion see Ostwald, *loc. cit.* (2) 27. 24—31.

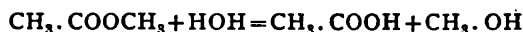
<sup>3</sup> *loc. cit.* (2) 16. 422. See also *post*, par. 227.

that of the base,  $c$  being a constant. Hence  $\frac{k}{k'} = \frac{\alpha^2}{\alpha'^2}$ ; and as  $\alpha$  and  $\alpha'$  depend (probably) only on the nature of the acids, and measure their affinities, it follows that the values of these affinities are as the square roots of the velocities of the reactions wherein the acids take part<sup>1</sup>.

The relative affinities of the various acids employed in this investigation are then calculated from the observed velocities, that of hydrochloric acid being taken as 100. The results agree very fairly with those formerly obtained (see *post*, par. 235). It is to be remembered that both series of numbers are affected by the occurrence of secondary changes in the chemical operations from the study of which they were deduced.

We have already learned (*ante*, chap. II. par. 187) that the molecular theory of chemical action points to a close connection between the rates at which chemical changes proceed, and the affinities (using this term in a wide sense) of the reacting bodies. This connection is now seen to be emphasised, and rendered exact, by the more purely dynamical studies based on Guldberg and Waage's theory of affinity<sup>2</sup>.

224. These studies are continued, with similar results, in Ostwald's next paper, where the operation represented by the equation



is selected for investigation, as being simple, and also typical<sup>3</sup>. The change proceeds at different rates in the presence of different acids. The action of the acids belongs to the class known as contact or catalytic actions (see *ante*, chap. II. par. 178).

Ostwald has carefully examined this process, using various acids, varying the time of action, &c., and has convinced himself that the operation is in all cases of the same kind,

<sup>1</sup> For a fuller treatment of this part of the subject see Ostwald, *loc. cit.* (2) 27. 35—36.

<sup>2</sup> We have here an instance of the merging into one, of the two paths of chemical advance.

<sup>3</sup> *loc. cit.* (2) 28. 449.

and that the same formula for finding the amount of methylic acetate decomposed may always be used, viz.

$$\log \frac{b}{b-x} = c \cdot a \cdot t, \text{ or, } \log \frac{1}{1-\frac{x}{b}} = c \cdot a \cdot t,$$

where  $a$  = amount of acid,  $b$  = amount of ethereal salt at the beginning of the reaction, and  $x$  = amount of this salt decomposed in time  $t$ ,  $c$  being a constant<sup>1</sup>.

The action is completed and equilibrium established in 24 hours; it is not however always necessary to carry the process to this final state, inasmuch as it can be shewn (and this is verified by experiment) that the final state is reached after a period ten times as long as that during which 50 per cent. of the ethereal salt is decomposed<sup>2</sup>.

225. Having thus satisfied himself as to the general character of the reaction which occurs in the catalytic decomposition of methylic acetate by acids in presence of water, Ostwald proceeds to study the influence exerted on the velocity of the change by varying the acids employed. His results are tabulated (pp. 472—486) and the square roots of the different velocity-coefficients are given in terms of that of hydrochloric acid as 100. The affinities of the acids as thus obtained are represented by larger numbers than those arrived at by the use of equilibrium-methods (see table *loc. cit.* p. 487; also *post*, par. 235). But this apparent increase in the values of these affinities is shewn to be due to secondary actions, between methylic acetate and water, which occur in the process in question. Nevertheless, the two series of numbers exhibit the closest parallelism even in small details.

226. In a later communication<sup>3</sup>, Ostwald shews that the 'inversion' of cane sugar in presence of various acids follows the same course as the change of methylic acetate into alcohol and acid. He employs the formula already given, viz.

$$\log \frac{1}{1-\frac{x}{b}} = c \cdot a \cdot t, \text{ or } \log \frac{b}{b-x} = c \cdot a \cdot t.$$

<sup>1</sup> See *loc. cit.* (2) 28. 451—472 for details regarding this formula and the ways in which Ostwald has tested its validity.

<sup>2</sup> *loc. cit.* (2) 28. 452—453.

<sup>3</sup> *loc. cit.* (2) 29. 385.

The values obtained for  $\log \frac{b}{b-x}$  are multiplied by 1000 to avoid fractions.

The quotient obtained by dividing these values by the time of action should be a constant quantity; this constant,  $c = \log \frac{b}{b-x} / a.t.$ , Ostwald calls the inversion- (or velocity-) constant. The results shew that the observed variations in the values of this quantity are very small, and are such as may be fairly attributed to errors of experiment (*loc. cit.* p. 401).

The square roots of the velocity-constants represent the relative affinities of the acids employed. The numbers obtained from this investigation agree very closely with those deduced from the experiments with methylic acetate; see table, par. 235.

In this paper Ostwald gives a table shewing the values of  $\log \frac{b}{b-x}$ , or  $\log \frac{1}{1 - \frac{x}{b}}$ , for all values of  $\frac{x}{b}$  between

0.001 and 0.999, to facilitate the calculations of those who may investigate the velocity-constants of various reactions.

227. From all these researches, Ostwald concludes that each acid, and each base, possesses a specific affinity-constant; and that all the chemical reactions in which the acid, or base, plays a part are determined by the magnitude of this constant. The researches on the decomposition of acetamide, and of methylic acetate, by water in presence of acids, have shewn that changes wherein 'predisposing affinity' and 'catalytic actions' are factors, are conditioned by the affinity-constants of the acids, as determined by the application of Guldberg and Waage's theory. And the researches on the action of acids on insoluble salts (see *ante*, par. 220) have shewn that the influence exerted by the *stability* of such salts on the equilibrium of the system is of the same kind as that exerted by the affinities of the reacting substances. Some of Ostwald's pupils have recently shewn that the solvent actions of various dilute acids on cream of tartar, and on the sulphates

of barium, strontium, and calcium, obey the same law ; each acid acts in accordance with its mass and its specific affinity-constant<sup>1</sup>.

228. The questions thus partly solved by Ostwald have been attacked by J. Thomsen by thermochemical methods.

When two, or more, acids and one base react in equivalent quantities, in a dilute aqueous solution, what are the proportions in which the acids combine with the base ? Measurements of thermal changes must, it would seem, throw light on this question. The process evidently is one wherein an equilibrium is established. Can the distribution of the masses of the acting bodies be deduced from measurements of the thermal gains or losses which accompany this distribution ?

229. Thomsen's method of attacking these questions rests upon the following considerations.

The various acids, by neutralisation with the same base, develop unequal quantities of heat. Now if one acid replaces another from its combination with a given base, the operation will be attended by a thermal change, which will be positive or negative according as the free acid, or the acid already combined with the base, possesses the greater heat of neutralisation. The extent of the reaction can be deduced from measurements of the thermal values of the different parts of the operation. Thus, take the reaction between nitric acid and sodium sulphate ; the thermal values of the following changes must be determined.

- (1) Neutralisation of sulphuric acid by soda.
- (2) Neutralisation of nitric acid by soda.
- (3) Decomposition of sodium sulphate by nitric acid.
- (4) Decomposition of sodium nitrate by sulphuric acid.
- (5) Action of sulphuric acid on sodium sulphate.
- (6) Action of nitric acid on sodium nitrate.
- (7) Action of sulphuric acid on nitric acid<sup>2</sup>.

<sup>1</sup> *J. für prakt. Chemie* (2) 29. 49.

<sup>2</sup> Thomsen, *Thermochemische Untersuchungen* 1. 98.

230. Now when nitric acid and sodium sulphate react, in equivalent quantities, in a dilute aqueous solution, heat is absorbed; but when sulphuric acid and sodium nitrate react, under similar conditions, heat is evolved. But the final distribution of the base between the two acids will be the same in both cases; and moreover this distribution will be the same as that which results when equivalent quantities of the two acids (sulphuric and nitric), and the base (soda) mutually react.

This statement may be put in a general form thus. Let the three bodies  $A$ ,  $B$ , and  $A'$  react in equivalent quantities, in a dilute aqueous solution; then,

$$\begin{aligned}[A, B, A'] &= [A, B] + [AB, A'] \\ &= [A', B] + [A'B, A];\end{aligned}$$

hence  $[A'B, A] - [AB, A'] = [A, B] - [A', B].$

Now if  $A = \text{SO}_3\text{Aq}$ ;  $B = \text{Na}_2\text{OAq}$ ; and  $A' = \text{N}_2\text{O}_5\text{Aq}$ ; it follows that

$$[\text{Na}^2\text{N}^2\text{O}^6\text{Aq}, \text{SO}^3\text{Aq}] - [\text{Na}^2\text{SO}^4\text{Aq}, \text{N}^2\text{O}^5\text{Aq}] = [\text{Na}^2\text{OAq}, \text{SO}^3\text{Aq}] - [\text{Na}^2\text{OAq}, \text{N}^2\text{O}^5\text{Aq}].$$

The differences between the thermal values actually observed were 4,144 and 4,080 gram-units respectively<sup>1</sup>.

When an equivalent of nitric acid ( $A'$ ) reacts on one equivalent of sodium sulphate ( $AB$ ) with decomposition of  $x$  equivalents of the latter salt, the final distribution of acids and base may be represented by the expression,

$$(1-x)AB + xA'B + xA + (1-x)A'.$$

And the total thermal change accompanying this operation will consist of the following partial changes;

(a) that attending the decomposition of  $x$  equivalents of  $AB$ , i.e.  $\text{Na}_2\text{SO}_4$ ;

(b) that attending the formation of  $x$  equivalents of  $A'B$ , i.e.  $\text{Na}_2\text{N}_2\text{O}_6$ ;

<sup>1</sup> *loc. cit.* p. 112.

(c) that attending the reaction of  $x$  equivalents of the acid  $A$ , i.e.  $H_2SO_4$ , on  $(1-x)$  equivalents of the salt  $AB$ ;

(d) that attending the reaction of  $(1-x)$  equivalents of the acid  $A'$ , i.e.  $HNO_3$ , on  $x$  equivalents of the salt  $A'B$ ; and

(e) that attending the reaction of  $x$  equivalents of the acid  $A$  on  $(1-x)$  equivalents of the acid  $A'$ .

The total thermal change may therefore be expressed by the formula,

$$[AB, A'] = x[(A', B) - (A, B)] + [(1-x)AB, xA] + [xA'B, (1-x)A'] + [(1-x)A', xA]^1.$$

231. Values have been found by Thomsen for all the partial thermal changes, except the last, the value of which is so small that it cannot be accurately determined, and may therefore be omitted from the calculation.

The following data, required for determining the values of the reactions (a), (b), (c), are the results of a large series of measurements made by Thomsen<sup>2</sup>.

#### DATA FOR REACTION (a).

(1)  $[Na^2OAq, SO^3Aq] = 31,378$ .

(2)	$n$	$[Na^2SO^4Aq, nN^2O^5Aq]$
	$\frac{1}{8}$	- 904
	$\frac{1}{4}$	- 1616
	$\frac{1}{2}$	- 2584
	1	- 3504
	2	- 4052
	3	- 4100.

The complete decomposition of  $Na_2SO_4$  into  $Na_2N_2O_6$  is attended with the absorption of 4144 gram-units of heat.

(3)	$y$	$[Na^2SO^4, ySO^3Aq, 2N^2O^5Aq]$
	0	- 4052
	1	- 1956
	2	- 1328
	3	- 1040.

<sup>1</sup> *loc. cit.* p. 113.

<sup>2</sup> *loc. cit.* pp. 99-110.



(4)	$\beta$	$[\frac{1}{3}\text{Na}^2\text{SO}^4, \frac{1}{3}\text{Na}^2\text{N}^2\text{O}^6\text{Aq}, \beta\text{N}^2\text{O}^6\text{Aq}]$
	$\frac{1}{3}$	- 1092
	$\frac{1}{2}$	- 1522
	1	- 1936.

## DATA FOR REACTION (b).

$$(1) [\text{Na}^2\text{OAq}, \text{N}^2\text{O}^6\text{Aq}] = 27,234.$$

(2)  $[\text{Na}^2\text{N}^2\text{O}^6\text{Aq}, \text{N}^2\text{O}^6\text{Aq}] = -78$  (as this is so small it is neglected in the calculations).

(3)	$n$	$[\text{Na}^2\text{N}^2\text{O}^6\text{Aq}, n\text{SO}^3\text{Aq}]$
	1	576
	2	758.

## DATA FOR REACTION (c).

$n$	$[\text{Na}^2\text{SO}^4\text{Aq}, n\text{SO}^3\text{Aq}]$
$\frac{1}{3}$	- 792
$\frac{1}{2}$	- 1262
1	- 1870
2	- 2352
4	- 2682.

The following approximate formula is deduced for finding the thermal value of this reaction for any value of  $n$ :

$$[\text{Na}^2\text{SO}^4\text{Aq}, n\text{SO}^3\text{Aq}] = -\frac{n}{n+0.8} 3300.$$

232. Substituting the chemical formulæ of the various bodies, and the actually observed thermal values, in the equation in par. 230, p. 435, we have this result:

$$[\text{Na}^2\text{SO}^4\text{Aq}, \text{N}^2\text{O}^6\text{Aq}] = x[\text{N}^2\text{O}^6\text{Aq}, \text{Na}^2\text{OAq}] - [\text{SO}^3\text{Aq}, \text{Na}^2\text{OAq}] \\ + (1-x) \left[ \text{Na}^2\text{SO}^4\text{Aq}, \frac{x}{1-x} \text{SO}^3\text{Aq} \right]$$

(the thermal values of the other parts are so small that they are omitted)

$$= -x \cdot 4144 + (1-x) \left[ \text{Na}^2\text{SO}^4\text{Aq}, \frac{x}{1-x} \text{SO}^3\text{Aq} \right] \\ = -3504.$$

Then, from the actually observed thermal values of the reaction between  $\text{Na}_2\text{SO}_4\text{Aq}$  and  $n\text{SO}_3\text{Aq}$  (see data for reaction (c)), a value must be sought for  $x$  which shall give a result in agreement with the total thermal value of the

change, which value is  $-3504$ . If  $x$  is taken as equal to  $\frac{2}{3}$ , we get this result:

$$\begin{aligned} [\text{Na}^2\text{SO}^4\text{Aq}, \text{N}^2\text{O}^6\text{Aq}] &= -\frac{2}{3} \cdot 4144 + \frac{1}{3} [\text{Na}^2\text{SO}^4\text{Aq}, 2\text{SO}^3\text{Aq}] \\ &= -\frac{2}{3} \cdot 4144 - \frac{1}{3} \cdot 2352 \\ &= -3547. \end{aligned}$$

The difference between the observed and calculated values is only about 1·25 per million of the heat of neutralisation. The thermal value of the reverse action, that namely between sulphuric acid and sodium nitrate, is found by the equation,

$$[\text{Na}^2\text{N}^2\text{O}^6\text{Aq}, \text{SO}^3\text{Aq}] = (1-x) 4144 + (1-x) \left[ \text{Na}^2\text{SO}^4\text{Aq}, \frac{x}{1-x} \text{SO}^3\text{Aq} \right] = 598.$$

The observed value was 576; the difference does not amount to more than 7 per million of the heat of neutralisation.

233. From these results, Thomsen draws the following conclusions.

(a) When soda, nitric acid, and sulphuric acid mutually react in equivalent quantities, in a dilute aqueous solution, two-thirds of the soda combines with the nitric acid, and one-third with the sulphuric acid.

(b) The final division of the base between the two acids is the same whether the soda were originally present as sulphate or nitrate<sup>1</sup>.

(c) The striving of the nitric acid to saturate itself with the base (*das Bestreben sich mit der Basis zu sättigen*), is twice as great as that of the sulphuric acid. Nitric acid, in aqueous solution, is therefore a stronger acid than sulphuric<sup>2</sup>.

This striving of the acids towards neutralisation, Thomsen calls the *avidity* of the acids. The expression evidently conveys exactly the same meaning as the term affinity in Ostwald's nomenclature.

234. Applying the method sketched above to the case of hydrochloric and sulphuric acids reacting on soda, Thomsen gets the following result:

$$[\text{Na}^2\text{OAq}, \text{H}^2\text{Cl}^2\text{Aq}] = 27,480.$$

<sup>1</sup> The truth of this statement has already been assumed (par. 230).

<sup>2</sup> *loc. cit.* p. 114.

Let  $A = \text{SO}_3\text{Aq}$ ;  $B = \text{Na}_2\text{OAq}$ , and  $A' = \text{H}_2\text{Cl}_2\text{Aq}$ ; and let  $x = \frac{2}{3}$ .

See equation par. 230.

Then  $[\text{Na}^2\text{SO}^4\text{Aq}, \text{H}^2\text{Cl}^2\text{Aq}] = -\frac{2}{3} \cdot 3898 - \frac{1}{3} \cdot 2352 = -3383$  :  
observed, -3364.

And  $[\text{Na}^2\text{Cl}^2\text{Aq}, \text{SO}^3\text{Aq}] = +\frac{1}{3} \cdot 3898 - \frac{1}{3} \cdot 2352 = 515$  : observed, 488.

The differences between the observed and calculated numbers amount to less than 1 per million of the heat of neutralisation.

Hence, the *avidity* (affinity) of hydrochloric acid for soda is equal to that of nitric acid, and is twice as great as that of sulphuric acid for the same base<sup>1</sup>.

Thomsen has determined the relative avidities (affinities) of many acids by this thermochemical method; his results are given in the table on p. 441.

Thomsen then applies the theory of Guldberg and Waage to his results<sup>2</sup>, and shews that the numbers obtained by experiment agree very well with those calculated by the use of equations deduced from this theory.

235. The following table contains Ostwald's results regarding the relative affinities of acids.

The numbers in column I are those obtained by the study of the inversion of sugar by various acids.

The numbers in column II are those obtained by the study of the decomposition of methylic acetate by water in presence of acids.

The numbers in column III are those obtained by the study of the decomposition of acetamide by water in presence of acids.

The numbers in column IV are those obtained by measuring the volume-changes which occur when various acids and bases are mixed in equivalent quantities.

The numbers in columns V and VI are those obtained by studying the action of dilute acids on calcium oxalate<sup>3</sup>; those

<sup>1</sup> *loc. cit.* p. 115.

<sup>2</sup> *loc. cit.* pp. 118—124.

<sup>3</sup> The details of the investigation from which these numbers are obtained have not yet been published; the work has been conducted by one of Ostwald's pupils.

## RELATIVE AFFINITIES OF ACIDS. (OSTWALD.)

ACID	I sugar inversion	II methyl acetate	III acetamide	IV division of base between 2 acids	V acids on normal	VI CaC <sub>2</sub> O <sub>4</sub> ; 1-10 <sup>th</sup> nrm.
Hydrochloric	100	100	100	98	100	97.9
Hydrobromic	105.5	99.1	98	—	94.9	99
Hydriodic	—	98.1	—	—	—	—
Nitric	100	95.7	98	100	110	100
Chloric	101.8	97.2	—	—	103.6	99.8
Sulphuric	73.2	73.93	65.4	66	70	74.2
		<sup>1</sup> [104.56]				
Methyl sulphuric	—	100.37	—	—	—	—
Ethyl sulphuric	100	99.33	—	—	—	—
Propyl sulphuric	—	98.98	—	—	—	—
Isobutyl sulphuric	—	98.53	—	—	—	—
Amyl sulphuric	—	97.82	—	—	—	—
Ethyl sulphuric	95.4	98.94	—	—	—	—
Isethionic	95.9	98.87	—	—	—	—
Benzene sulphonic	102.2	99.54	—	—	—	—
Formic	12.4	11.49	5	3.9	2.59	12.9
Acetic	6.32	5.87	2.34	1.23	1.05	7.35
Propionic	—	5.51	—	1.04	—	—
Butyric	—	5.47	—	0.98	—	—
Isobutyric	5.79	5.18	—	0.92	—	—
Monochloracetic	22	20.8	13	7	5.1	21.3
Dichloracetic	52.1	48	40.8	33	18.3	48.8
Trichloracetic	86.8	82.6	80	80	64.2	89.9
Glycollic	11.4	—	—	—	—	—
Diglycollic	16.3	—	—	—	—	—
Lactic	10.3	9.49	5	3.3	4.1	13.3
Methoxyacetic	13.5	—	—	—	—	—
Ethoxyacetic	11.7	—	—	—	—	—
Methoxypropionic	11.8	—	—	—	—	—
Hydroxyisobutyric	10.3	9.60	—	—	—	—
Trichlorolactic	—	26.3	—	—	—	—
Pyruvic	25.5	25.9	—	—	—	—
Oxalic	43	43	22.6	—	—	—
Malonic	17.5	16.9	—	—	—	—
Glyceric	13.1	—	—	—	—	—
Succinic	7.38	7.04	2.5	1.45	2.05	9.3
Malic	11.3	10.86	4.7	2.82	5.05	12.05
Tartaric	—	15.15	7.5	5.2	(?) 4.62	14.16
Pyrotartaric	10.3	—	—	—	—	—
Racemic	—	15.15	—	—	—	—
Citric	13.1	12.79	4	—	3.06	14.44
Phosphoric	24.9	—	—	—	—	—
Arsenic	21.9	—	—	—	—	—

<sup>1</sup> The affinity of sulphuric acid appears less than that of its derivatives obtained by replacing hydrogen by indifferent, or even basic, radicles. But it is to be noted that  $\frac{1}{2}$  H<sub>2</sub>SO<sub>4</sub> is compared with SO<sub>2</sub> · OH · OCH<sub>3</sub> &c. If molecular quantities are

in V represent the results of the use of normal solutions, and those in VI of  $\frac{1}{10}$ th normal solutions of acids.

The numbers in column I are regarded by Ostwald as the most trustworthy; the reaction employed is freer from secondary actions than any of the others. The numbers in column II are also very satisfactory; the reaction used ( $\text{CH}_3\text{.COO.CH}_3 + \text{HOH} = \text{CH}_3\text{.COOH} + \text{CH}_3\text{.OH}$ ) was simpler than any of those by which the numbers in the succeeding columns were obtained; the acids whose affinity-constants were sought for remained in the free state throughout the whole process, so that no complication could arise from the formation of acid salts, &c. such as occurred in the processes investigated in columns III to VI. There was only one secondary action, namely, that due to the presence of free acetic acid, and the influence of this could be partially eliminated in the calculations.

The two series of numbers obtained by employing the reaction of acids on solid calcium oxalate differ greatly, but the arrangement of the acids in accordance with their affinities is the same in both. The numbers obtained by using dilute acids ( $\frac{1}{10}$ th normal), column VI, agree very well with those in column II, while the numbers deduced from observations with stronger solutions (normal), column V, agree better with those based on measurements of volume-changes, column IV; hence, Ostwald argues, the explanation before given regarding the combined action of water and acid on calcium oxalate is confirmed. When very dilute solutions of acids are employed, the water exerts an action on the solid salt independently of the acid, just as in the reaction from which the numbers in column II are obtained there is a twofold action, partly due to the water and partly to the acid. It will still be necessary to endeavour to separate these actions before numbers are obtained which represent the affinity-constants of the acids alone. From experiments not yet published, Ostwald thinks that the numbers obtained by studying the division of bases between two acids are affected by a source of error which

to be compared, the observed numbers for sulphuric acid reactions must be doubled; if this is done the affinity of this acid is 104.56.

makes the stronger acids appear stronger, and the weaker acids weaker, than they really are (*loc. cit.* (2) 29. 403).

The results obtained by thermochemical methods are presented in the following table.

RELATIVE AFFINITIES (*avidities*) OF ACIDS. (THOMSEN<sup>1</sup>.)

Acid.		Acid.	
Nitric	100	Oxalic	24
Hydrochloric	100	Orthophosphoric	13
Hydrobromic	89	Monochloracetic	9
Hydriodic	79	Hydrofluoric	5
Sulphuric	49	Tartaric	5
Selenic	45	Citric	5
Trichloracetic	36	Acetic	3

236. We have already seen that from his volumetric experiments on the division of a base between two acids, Ostwald concluded that the true relative affinities of hydrochloric, nitric, and sulphuric acids are independent of the nature of the base (see *ante*, par. 223). If this holds good for all acids, the conclusion is arrived at that the relative affinities of bases are independent of the nature of the acids on which they react.

Stating the absolute affinity of an acid  $A$ , for a base,  $C$ , in the form  $f(A, C)$ , the statement just made may be put thus

$$f(A, C) = \phi(A), \psi(C):$$

that is, the affinity between an acid and a base is the product of the specific affinity-constant of the acid, and the specific affinity-constant of the base<sup>2</sup>.

This conclusion is confirmed, on the whole, by Thomsen's thermochemical researches. It was mentioned in pars. 222—3 that Ostwald had developed Guldberg and Waage's fundamental equation for finding the velocity of a chemical change,

<sup>1</sup> *loc. cit.* 1. 308. The numbers given by Thomsen are calculated for equivalent weights of the various acids (e.g. for  $\text{HCl}$ ,  $\frac{1}{2} \text{H}_2\text{SO}_4$ ,  $\frac{1}{3} \text{H}_3\text{C}_6\text{H}_5\text{O}_7$ , &c.), except in the case of phosphoric acid; the number given in the table for this acid is taken from L. Meyer (*Die modernen Theorien*, p. 489). The chapter on *Chemische Massenwirkung* in L. Meyer's book should be studied in conjunction with the preceding paragraphs (203—235).

<sup>2</sup> Ostwald, *loc. cit.* (2) 16. 425.

so as to separate the factors  $k$  and  $k'$  (in reactions between acids and bases) into two parts, one depending solely on the nature of the acid and the other solely on the nature of the base, and that he had thence deduced the conclusion that the affinity-constants of acids are proportional to the square roots of the velocities of the reactions brought about by them.

Reviewing the whole of the work on affinity which has passed before us, we are I think justified in assenting to Ostwald's conclusion that the specific intensity of any action brought about by an acid is conditioned by the value of the affinity of that acid; or as it is put by Ostwald in another paper (*loc. cit.* (2) 29. 57), the affinity-values of the acids appear as constants which quantitatively condition the chemical actions of these acids. The numbers hitherto obtained representing the relative magnitudes of these affinities can be regarded only as approximate; no reaction has yet been found entirely free from secondary changes, nor has it been possible completely to eliminate the influence of these secondary changes in making the necessary calculations. Nevertheless we may use the numbers given by Ostwald, more especially those derived from his study of the accelerating action of various acids on the decomposition of methylic acetate by water, and on the inversion of sugar solutions, in endeavouring to find the velocities, and final states of equilibrium of many chemical reactions.

237. Guldberg and Waage did not attempt to do more than find the coefficients of affinity of various reactions. In their use of the expression, a coefficient of affinity is the resultant of the actions of many forces; Ostwald has analysed this quantity, and has endeavoured to assign to each member of the changing system a definite number which represents the share of the total result belonging to that constituent. As each element has a definite atomic weight, and each atom has a definite valency, and as these numbers sum up a great deal of information regarding the properties of the element and its compounds when looked at from a statical point of view; so each chemical substance appears to have a definite

affinity-constant, and this number conveys much information regarding the substance when regarded from a kinetical stand-point. These affinity-constants are true equivalents; they express power of doing definite amounts of chemical work. It was for such numbers that Bergmann sought, but sought in vain; they have at last been found, or, at any rate, we have been shewn how they are to be found, by following in the steps of Bergmann's great opponent, Claud Louis Berthollet<sup>1</sup>.

## SECTION 2. *Thermal and other methods of studying affinity.*

238. The subject of affinity has thus far been considered, for the most part, apart from any kinetic theory of chemical action. But it is scarcely possible to be satisfied with this treatment. We cannot but attempt to form some mental image of the molecular and atomic mechanism of the changes which are conditioned by the affinities of bodies exerting chemical action on each other. Is affinity, in the last analysis, to be ascribed to attractions between atoms; or is it due to the electrical conditions of different atoms? How far do measurements of the quantities of heat evolved, or absorbed, during chemical operations, afford an insight into the nature of these processes? Questions of this kind cannot be overlooked, however difficult, or even impossible, it may be at present to answer them.

239. The attempts which have been made to apply the data of thermal chemistry to the problems of affinity have generally been based on the hypothesis, that affinity is an attraction between atoms which is dependent on variations in the potential energies of these atoms. On this hypothesis, the thermal changes which accompany definite chemical processes may be regarded as affording measurements of the change of potential into kinetic energy which proceeds along with the rearrangement of the atoms of the elements constituting the chemical systems.

<sup>1</sup> Compare Mills, *Phil. Mag.* (5) 1. 13. with Ostwald, *Journal für prakt. Chemie* (2) 29. 57.



But even if this is granted, it is at present impossible to make much use of this means of measuring the energy-change in question.

Take a simple case. Given the heat evolved during the change of 2 parts by weight of gaseous hydrogen and 16 parts of oxygen into 18 parts of liquid water, we have the difference between the energies of the two systems, (1) gaseous  $H_2 + O$ , and (2) liquid  $H_2O$ , as measured by the amount of heat appearing in the calorimeter. But a part of the energy-difference, as thus determined, is due to the change of gaseous into liquid water, and another part to the contraction which occurs when two volumes of hydrogen and one of oxygen combine to produce two volumes of water-gas<sup>1</sup>.

In the majority of chemical operations, the physical changes are more complex than in this instance. Different fractions of the total quantities of heat measured by the calorimeter are connected with changes in the densities, the crystalline forms, the thermal capacities, or generally, with changes in the *disgregation*<sup>2</sup> of the substances taking part in the chemical processes for which thermal values are required. But we are not, generally speaking, able to measure the thermal change which accompanies a disgregation-change. Indeed we cannot always decide whether the value of this part of the total thermal change is equal to, greater, or less than, the value of that part which measures the affinities of the chemically reacting substances<sup>3</sup>.

<sup>1</sup> For methods of calculating these two parts of the total loss of energy see Naumann, *Thermochemie* 217—219; and also Lothar Meyer, *loc. cit.* 430—434.

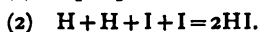
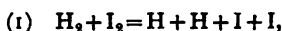
<sup>2</sup> Clausius, *Pogg. Ann.* 116. 79, &c. Disgregation is a quantity depending on the arrangement in space of the molecules of a substance; it expresses to what extent the separation of the molecules, which is brought about by the action of heat, has been accomplished. The disgregation of a body is greater in the gaseous than in the liquid, and greater in the liquid than in the solid state. The disgregation may change without an alteration of the chemical composition or the physical state of the body; thus, when a gas expands, its disgregation increases. As a rule, disgregation increases when the distance between the molecules of a substance is increased. Compare Horstmann, *Annalen*, 170. 195; also Naumann, *loc. cit.* 209. L. Meyer (*loc. cit.* 429) considers *Disgregation* as equivalent to degree of division (*Vertheilungsgrad*).

<sup>3</sup> Favre and Valson's experiments shew that the thermal changes attending the contraction of solutions in which various salts are formed and dissolve, are very

240. Even in cases of dissociation, brought about by the supply of energy in the form of heat, it is not at present possible to separate the energy used in effecting disgregation-changes from that entirely employed in separating the molecules into less complex molecules, or into atoms.

But even if this could be done, a difficulty would still remain.

Take the formation of gaseous hydriodic acid from gaseous hydrogen and iodine; the purely chemical reaction is not fully represented by the statement,  $H + I = HI$ , but rather by the equation,  $H_2 + I_2 = 2HI$ , which is divisible into two parts;



The problem presented is, to measure the energy-change which accompanies the second part of this chemical change. But the calorimetric determinations hitherto made furnish no means for separating the total thermal value into its constituent parts. A number is obtained which is the sum of two quantities neither of which is known.

241. But there is a more far-reaching objection to many of the conclusions regarding affinity which have been drawn from thermal measurements. It is, to say the least, improbable, that affinity consists of an attraction between atoms, depending on the energy of position of these atoms. The atoms of which a molecule is composed must be regarded as in motion within the molecule; but of the nature of this

large. See Watts's *Dict.* 2nd Suppl. 292 *et seq.*; and 3rd Suppl. 983. See also for more details *Die modernen Theorien der Chemie*, (4th ed.) p. 436.

Berthelot's 'law of maximum work' (see book I. chap. IV. par. 133) is based on the assumption that affinity is a form of potential energy. Meyer shews that there are cases where this law cannot hold good, even when we assume that all actions, other than the attractions between atoms, are eliminated. For a fuller discussion of the connections between this law and affinity see L. Meyer, *loc. cit.* pp. 440—460. That a degradation of energy is an invariable accompaniment of a chemical action, occurring by itself, is certain, but it is not the case that an operation involving degradation of energy necessarily occurs. A chemical change between gases, involving degradation of energy, may be rendered impossible by causing the gases to expand, and this although the total heat evolved during the operation is almost the same whether the gases are expanded or condensed. See Lord Rayleigh, *Proc. R. I.* March 5, 1875.

motion we know little or nothing. A feasible hypothesis is that the motion is such as produces a constant change of potential into kinetic energy, and *vice versa*. But if this view is adopted, the same compound will be more or less ready to undergo chemical change, according to the *phase* (see *ante*, chap. II. par. 193, p. 395) in which it is. Let  $AB$ , a diatomic molecule of a gas, collide with  $C$ , a monatomic molecule of a gas; more than one change may occur;  $AC$  and  $B$  may be produced although the affinity of  $C$  for  $A$  is less than that of  $C$  for  $B$ . The motions of the atoms, and hence the relations between their potential and kinetic energies at any moment, will be conditioned by the temperature, among other causes. In cases more complex than that just considered, e.g. in the reactions between two diatomic gaseous molecules,  $AB$  and  $CD$ , it is not at present possible to separate the action of heat, in bringing the molecules into phases whereat chemical change occurs, from the action of affinity pure and simple.

242. Thus, we come back to the statement, already insisted on in book I., that there is no essential difference of kind between so-called endothermic and exothermic actions<sup>1</sup>.

Until there is a more definite kinetic theory of affinity than has yet been proposed, it will not be possible to apply thermal methods, except in a general and broad way, to the questions suggested by the term affinity.

243. Every chemical change involves a degradation of energy, but chemical energy, of whatever form, cannot be entirely run down into heat.

This subject has been considered by Helmholtz<sup>2</sup>.

The action of chemical forces gives rise not only to heat, but also to other forms of energy, and, in the latter cases,

<sup>1</sup> See I. Meyer, *loc. cit.* 447—448. Compare also book I. chap. IV. pars. 119, and 133; also book II. chap. II. section 2, especially par. 193. Thomsen's 'Theoretische Betrachtungen über die Dynamik der chemischen Prozesse,' in *Thermochemische Untersuchungen* 2. 468—474, should also be carefully studied. See also in connection with this, Rathke, *Über die Principien der Thermochemie, und ihre Anwendung* (Halle, 1881). There is also an abstract of an interesting paper by Potilitzin in *Ber.* 14. 2044.

<sup>2</sup> 'Die Thermodynamik chemischer Vorgänge,' *Sitzber. der Wiss. Akad. zu Berlin*, 1882; see *Wissenschaftliche Abhandlungen*, 2. 958.

sometimes without a change of temperature bearing any kind of relation to the magnitude of the actions between the changing substances; e.g. in the performance of work by the battery. Hence, we must distinguish, in chemical processes, between those parts of the chemical energy which are freely changeable into other forms, and those which can only be produced in the form of heat. The former is called, by Helmholtz, the *free energy*, the latter the *bound energy* (*freie und gebundene Energie*). The *bound energy* is the difference between the total internal energy and the free energy. Changes proceeding of themselves from a state of rest, and at a uniform temperature, without the help of energy from without the system, can only proceed in directions such that the free energy decreases. Assuming the universality of the second law of thermodynamics, it follows that the direction in which the chemical affinity of a substance can act depends on the value of the free energy, and not on that of the total energies which make themselves known by the production of heat. The free energy can only be calculated in completely reversible changes. Electrolytic decompositions with unpolarised electrodes serve well for this purpose; indeed it was when examining the relations between the electromotive force of such cells and the chemical changes which proceed within them that Helmholtz was led to the conception of free chemical energy.

In all isothermal changes work is done only at the cost of the free energy; in all adiabatic changes work is produced at the cost both of the free and the bound energy of the system. In all other cases, external work is carried on at the cost of the free energy, and loss of heat at the cost of the bound energy; and for every rise of temperature of the system, free is changed into bound energy. This last case may occur in irreversible processes, so that free energy is changed into kinetic energy which again may be converted, by friction, &c., either wholly or in part into heat. In such a case the heat evolved in the change from the initial to the final state of the system represents the difference between the total internal energies of the system. Now this difference is the quantity

measured in investigations of thermal changes accompanying chemical processes; but the work done by the free energies of the system, the free work (*freie Arbeit*), which determines the direction of the chemical change, is different from this, and cannot be measured by merely finding the total quantity of heat evolved.

244. But it may be admitted that chemical affinity, considered as some form of atomic energy, cannot as yet be satisfactorily measured by thermal methods, and at the same time it may be held that thermal measurements do throw light on the differences between the affinities of substances in various analogous reactions, using the term affinity in a sense similar to that wherein it is employed by Guldberg and Waage.

Thus, let us compare the thermal values of the reactions which occur in the formation of gaseous hydrochloric, hydrobromic, and hydriodic acids from gaseous hydrogen, and gaseous chlorine, gaseous bromine, and gaseous iodine respectively<sup>1</sup>. The change is expressed in thermal notation as  $[H, X]$ ; the following are the numbers to be compared,

$[H, X]$  gaseous.

$X = Cl = 22,000$  gram-units +.

$X = Br = 12,000$  „ +.

$X = I = 1,530$  „ -.

Are the affinities of Cl, Br, and I for H in the proportion of the numbers 22 : 12 : - 1·5 ?

When the reaction is written, as our former study of chemical changes has taught it ought to be written, in the form  $[H^2, X^2] = 2[H, X] - [H, H] - [X, X]$ , we see that the numbers given do not measure the affinities of the atoms of chlorine, bromine, and iodine for that of hydrogen. We have at present no means for measuring the absorptions and evolutions of heat the sums of which are represented by the numbers 22,000, 12,000, and - 1530. We are not even justified in concluding that the value  $-[X, X]$  is the same whether  $X = Cl, Br, \text{ or } I$ ; indeed experiments on the densities

<sup>1</sup> Compare Jahn, *Die Grundsätze der Thermochemie*, 35—43.

of these gases at high temperatures rather tend to shew that this assumption is untenable. But if the term affinity is used as meaning the resultant of the actions of the various forces which come into play in any chemical change, eliminating as far as possible actions which are manifestly physical, then I think we may say that the differences between the affinities concerned in the three strictly comparable reactions, viz. formation of gaseous hydrochloric, hydrobromic, and hydriodic acids, from their gaseous elements, are expressed by the differences between the numbers 22, 12, and  $-1\cdot5$ .

245. If this conclusion is sound, then the differences between the thermal values of analogous chemical changes in which the same elements take part should be capable of being represented as multiples of a common number.

Here are some data suited for our purpose.

$$(1) [H, X, Aq]; X = Cl = 39,315 : X = Br = 28,370 : X = I = 13,170 \text{ grm.-units} +.$$

$$\therefore [H, Cl, Aq] - [H, Br, Aq] = 10,945,$$

$$\text{and } [H, Cl, Aq] - [H, I, Aq] = 26,145.$$

$$(2) [K, X, Aq]; X = Cl = 101,170 : X = Br = 90,230 : X = I = 75,020 \text{ grm.-units} +.$$

$$\therefore [K, Cl, Aq] - [K, Br, Aq] = 10,940,$$

$$\text{and } [K, Cl, Aq] - [K, I, Aq] = 26,150.$$

$$\text{Also } [Na, Cl, Aq] - [Na, Br, Aq] = 10,930,$$

$$\text{and } [Na, Cl, Aq] - [Na, I, Aq] = 26,150.$$

The difference between the heat of formation, in solution, of a chloride and an analogous bromide, is 10,940 units; and that between a chloride and an analogous iodide is 26,150 units.

Now these differences reappear in the following data.

$$\left. \begin{array}{l} [M, Cl_2, Aq] - [M, Br_2, Aq] = 2 \times 10,940 \\ \text{and } [M, Cl_2, Aq] - [M, I_2, Aq] = 2 \times 26,150 \end{array} \right\} \text{ when } M = Ca, Sr, \text{ or } Cu.$$

Here we notice a constant thermal value attending the substitution of one halogen by another, the metallic radicle being unchanged; now, if the halogen remain the same, is there a constant thermal value for the substitution of one metal by another, chemically analogous, metal?

The following data shew that there is such a constant thermal value.

$$[K, X, Aq] - [Na, X, Aq] = \begin{cases} 4,660 & \text{when } X = \text{Cl}, \\ 4,650 & \text{when } X = \text{Br}, \\ 4,620 & \text{when } X = \text{I}; \end{cases}$$

and  $[Sr, X^2, Aq] - [Ca, X^2, Aq] = 2 \times 4,020$  when  $X = \text{Cl}, \text{Br}, \text{or I}.$

The thermal values of another series of analogous reactions are given in the following table.

*Heats of oxidation of  $N_2O_2$ ,  $N_2O_3$ , and  $N_2O_4$ .*

$$[N^2O^4, Aq, O] = 18,320 \text{ gram-units} +.$$

$$[N^2O^3, Aq, O^2] = 2 \times 18,320 \quad \text{,,} \quad \text{,,}$$

$$[N^2O^2, Aq, O] = 2 \times 18,165 \quad \text{,,} \quad \text{,,}$$

$$[N^2O^2, Aq, O^2] = 3 \times 18,215 \quad \text{,,} \quad \text{,,}$$

$$[N^2O^2, Aq, O^2] = 4 \times 18,243 \quad \text{,,} \quad \text{,,}$$

The data presented in this paragraph justify the conclusion that a study of the thermal values of analogous chemical changes occurring between similar elements is fitted to throw light on the differences between the affinities of the substances taking part in these reactions.

246. The theory of vortex atoms promises to help towards a solution of the problem of affinity.

The theory has been applied to chemical combinations by J. J. Thomson<sup>1</sup>.

A compound molecule of a gas is regarded by this theory as consisting of two, or more, vortex rings. This united vortex ring will separate into its parts when subjected to a disturbing influence, such as the action due to other vortex rings in the neighbourhood. The theory thus leads to a conception of chemical combination closely resembling that enunciated by Williamson, and afterwards altered and developed by Pfaunder (chap. II. pars. 186, 187). But for a compound gas to be more than a mere mixture of elementary gases it is necessary that 'the mean time during which an atom is paired with another of a different kind, which we shall call the paired time,

<sup>1</sup> *On the motion of vortex rings.* The Adams Prize Essay for 1882. See especially p. 114 et seq.

'should be large, compared with the time during which it is 'alone and free from other atoms, which we shall call the 'free time' (*loc. cit.* p. 115).

The ratio of *paired* to *free* time will be diminished by any disturbance to which the gas is subjected; when the diminution is carried past a certain amount, the gas is decomposed. Now 'the pairing of two atoms.....is attended by a large 'increase in the translatory energy;' but as these atoms are only paired for a time, 'the whole increase in the translatory 'energy of a large number of molecules will depend.....on 'the ratio of the paired to the free times' of the vortex atoms which form the molecules of the substance (*loc. cit.* p. 116). The value of this ratio in the case of an elementary gas will to a great extent condition the chemical properties of that gas; it will also determine whether chemical combination shall or shall not occur between two gases, and if it occurs, it will fix the proportions between the amounts of the various compounds produced. An elementary gas will readily enter into chemical combination, only when the ratio of free to paired time is larger for the molecule of the element, than for that of the compound produced. The value of the ratio in question may therefore afford a measure of the relative affinities for each other of the atoms of various compound molecules<sup>1</sup>.

247. In the general remarks made on the subject of affinity in par. 202 it was said that attempts might be made to obtain measurements of affinities by electrical methods. I wish now to draw the student's attention to some of the more important of these attempts.

The views of Davy and of Berzelius regarding the connections between electrical and chemical actions have already been referred to (book I. chap. II. pars. 46 to 48).

Faraday discovered that when an electric current passes through an electrolytic cell, the amount of decomposition is definite for each element of the electrolyte, and is dependent on the quantity of electricity which is transmitted. Let  $\epsilon$  be the mass of an element separated from any of its salts by the

<sup>1</sup> For more details see J. J. Thomson, *loc. cit.*



passage of one unit of electricity. Then  $\epsilon$  is called the electrochemical equivalent of that element. Since unit quantity of electricity is transmitted by unit current in unit time, we may say that one electrochemical equivalent of an element is separated from any of its combinations by unit current in unit time.

The minute verification of this law is still being worked out experimentally.

In the course of his applications of the conception of the conservation of energy, Joule undertook a series of researches on the 'energetics' of the electric current<sup>1</sup>. The case of the passage of a current through a wire was considered, and the quantity of heat evolved was found to be expressed by the equation

$$H = CE,$$

where  $H$  is the quantity of heat developed per second, and  $C$  and  $E$  are the current and the electromotive force respectively.

Since Joule had himself shewn that heat is changeable into work, the equation took the form

$$W = JH = CE,$$

where  $J$  = the mechanical equivalent of heat.

The phenomena attending the evolution of heat during the passage of a current through an electrolyte were then examined by Joule, and it was shewn that the total quantity of heat could be separated into two parts. One part was expressible as the result of overcoming ordinary resistance in accordance with his previous law, and the other part was due to chemical changes in the cell. He then determined the quantity of heat evolved, during a given time, in a process of electrolysis by a current of given strength; then, by applying Ohm's law, and the law stated connecting heat with resistance and current, he found the heat which would have been evolved, had a wire with resistance equal to that of the electrolyte been substituted for the electrolyte. The difference between these two quantities of heat is, Joule said,

<sup>1</sup> *Phil. Mag.* 20. 98; 22. 204; and *do.* (2) 3. 481. See also the article 'Electricity' in *Encycl. Brit.* Vol. 8. (9th Ed.) pp. 88-92.

'equivalent to the heat which is due to the reverse chemical 'combination by combustion or other means' (*loc. cit.* (2) 3. 494).

248. The problem was further considered by Sir W. Thomson<sup>1</sup>. His reasoning was somewhat as follows.

Let unit quantity of electricity pass through a cell of infinitely small resistance; then, by Joule's law, the work done by the current is equal to  $E$ , the electromotive force. But 'e' gram of one of the elements of the electrolyte has been electrolysed, in accordance with Faraday's law. Let  $\theta$  be the quantity of heat developed by the combination of one gram of this element to reproduce the electrolyte, then, according to Thomson, since no work is expended in any other part of the circuit,

$$E = J\epsilon\theta, \text{ and therefore } \theta = \frac{E}{J\epsilon}.$$

To realise this equation in practice a great many corrections have to be applied.

This formula presents us with an electrical method for determining the heats of combination of various elements, or, we may say, the energy-changes attending the formation of various compounds. In Joule's papers, the values of the quantity represented by  $\theta$  were regarded as affording measures of 'the intensities of affinity' of different substances (*loc. cit.* 20. 99); but we have seen that this cannot now be held, except the term 'affinity' is used in a very wide sense.

249. Wright has applied Joule and Thomson's method of research, and has endeavoured to determine 'chemical affinity 'in terms of electromotive force'.

In Wright's use of the term, the 'affinity' between the constituents of a compound is measured by the work done in separating the compound into these constituents. This work can be measured by electrical methods; thus, Wright says, 'the affinity between the final products of an electrolyte, i.e. 'the work done in resolving it into these final products.....

<sup>1</sup> *Phil. Mag.* for December, 1851: see *Mathematical and Physical Papers* 1. 472.

<sup>2</sup> *Phil. Mag.* (5) 9. 237, 331: 11. 169, 261, 348: 13. 265: 14. 188: 16. 25. See also a general account of his work to the end of 1880 in *Chem. News*, 42. 249.

'is readily determinable, by determining the difference of potential subsisting between the electrodes, and the heat evolved as such, during the electrolysis of a gram-equivalent' (*Chem. News, loc. cit.*).

But in a process of electrolysis, the electrolyte is first separated into primary, or *nascent* products, which are such that their change into the secondary, or final products is attended with evolution of heat. The E.M.F. required to separate the electrolyte into the nascent products would therefore be numerically greater than the E.M.F. required to separate it into the final products. Moreover, the E.M.F. required to break up a given electrolyte, under given conditions, into the nascent products of electrolysis, varies, because of the occurrence of secondary physical and chemical actions between the electrodes and the dissolved gases, &c. Heat is generated in these secondary changes, and the energy thus produced diminishes the work that would otherwise be done by the current in effecting electrolysis. Hence the E.M.F. which corresponds to the total electrolytic work actually done by the current, is less than the constant amount which would be required were the process not complicated by secondary reactions<sup>1</sup>. Wright attempts to find the value of that part of the E.M.F. which corresponds to the secondary changes, (1) when none of the products of electrolysis are developed in the nascent state, and (2) when the products are entirely developed in this state<sup>2</sup>. The determination becomes very difficult in the latter case: if it can be successfully made, we shall have data for finding the E.M.F. produced by the combination of the constituents of certain compounds, starting with these constituents in the nascent state. But as the nascent state of a substance most probably represents its condition when the great majority of the molecules are separated into atoms, it follows that Wright's determinations of the two parts of the E.M.F. concerned in

<sup>1</sup> Wright, *Phil. Mag.* (5) 13. 265. For a short and clear statement of the whole of this subject, see Clerk Maxwell's *Elementary Treatise on Electricity*, pars. 182—192.

<sup>2</sup> See *Chem. News, loc. cit.* p. 253.

electrolytic decompositions, if successfully conducted, must throw considerable light on the actions of the forces which condition the combinations of atoms, and therefore, on the most profound parts of the problem of chemical affinity.

250. The subject of the connection between the forces which come into play in chemical and electrical phenomena, has been considered by Helmholtz in *the Faraday Lecture* for 1881<sup>1</sup>.

Faraday's statement that 'the equivalent weights of 'bodies are simply those quantities of them which contain 'equal quantities of electricity,.....or, if we adopt the atomic 'theory or phraseology, then the atoms of bodies which are 'equivalent to each other in their ordinary chemical action, 'have equal quantities of electricity naturally associated with 'them', is developed by Helmholtz in the light of modern conceptions of molecular structure.

Helmholtz regards each monovalent atom, or group of atoms, forming an *ion*, as moving about with an equivalent of electricity, each divalent atom (or ion) with two equivalents of electricity, and so on. An ion may be attracted to the surface of an electrode, and if the electromotive force is sufficient, the electric charge of the ion may be attracted, and so the ion may itself become electrically neutral. A gas, e.g. hydrogen, evolved during electrolysis is electrically neutral; this may be because each atom is electrically neutralised, or more probably, because neutrality is obtained by the union of one atom, with its positive charge, with another atom, carrying a negative charge of electricity. Helmholtz then shews by experiment that 'electrolytic conduction is not.....necessarily connected with 'a small resistance to the current;' and that 'the connection 'of electric and chemical force is not at all limited to the 'acid and saline solutions usually employed' (*loc. cit.* p. 293). But why is the electric attraction at the poles of a battery of, say, two Daniell's cells, so small, when this combination is nevertheless able to decompose water, a liquid in the forma-

<sup>1</sup> *C. S. Journal, Trans.* for 1881. 277.

<sup>2</sup> *Experimental Researches in Electricity*, Series VII. par. 869.

tion of 1 gram of which from its elements an amount of heat equal to 1,600,000 gram-metres of work is developed? Helmholtz finds the answer to this question in the enormous electrical charges of the elementary atoms. He calculates that 'the electricity of 1 milligram of water, separated and 'communicated to two balls, 1 kilometre distant, would produce an attraction between them equal to the weight of '26,800 kilograms;' or comparing 'the gravitation acting 'between two quantities of hydrogen and oxygen with the 'attraction of their electric charges,' the electrical force is 71,000 billion times greater than the gravitation force (*loc. cit.* pp. 293—294). A very small battery can decompose water, because the attracting force exerted by the poles on the enormous charges of the atoms of hydrogen and oxygen is very great.

Helmholtz shews by various experiments that an electromotive force as small as  $\frac{1}{1000}$  Daniell is able to attract the ions to the electrodes of a small cell, and to charge these electrodes as condensers. Indeed no phenomenon has been discovered which indicates any limit to the smallness of the electromotive force which is able to do this, and 'we must, 'therefore, conclude that no other force resists the motions of 'the ions through the interior of the liquid than the mutual 'attractions of their electric charges' (*loc. cit.* p. 297). The electric attraction produces an equal distribution of the opposite constituent atoms throughout the liquid, which is thus electrically as well as chemically neutralised.

But let the liquid be decomposed, there must be electrical attraction between the ions with their charges of electricity and the electrodes of the battery. If this attraction is not sufficient to deprive the ions of their charges, the cation is attracted to, and retained by the cathode, and the anion by the anode, with a force so great that no diminution of pressure over either electrode suffices to remove the ion. But 'increase 'the electric potential of the electrodes so that the electric 'force becomes powerful enough to draw the electric charge 'of the ions over to the electrode,' and the ions are liberated as gases, or diffuse into the liquid. If the ponderable matter

of the ions were attracted by the electrodes, this attraction would remain after discharge, but it does not, therefore 'we must conclude that the ions are drawn to the electrodes only 'because they are charged electrically' (*loc. cit.* p. 299).

The mechanism is then described whereby the electrical force is concentrated at the surface of electrodes, until, acting at molecular distances, it becomes able 'to compete with the 'powerful chemical forces which combine every atom with its 'electric charge, and hold the atoms bound to the liquid' (p. 300).

Helmholtz then develops the view that equivalents of positive and negative electricity (using the language of the dualistic hypothesis) are attracted by different atoms with different forces; e.g. the atom of zinc has probably a greater attraction for positive electricity than the atom of copper has for negative electricity. These attractive forces act only through molecular distances. This hypothesis of 'different 'degrees of affinity between the metals and the two electricities' explains the facts of contact electricity; e.g. the greater attraction of zinc for positive electricity than of copper for negative produces chemical decomposition of the electrolyte present, and electrical equilibrium is not possible until this decomposition is completed (*loc. cit.* pp. 300—302)<sup>1</sup>.

Each atom is thus regarded as charged with a definite 'equivalent of electricity.' A divalent atom has two equivalents, a trivalent atom three equivalents, and so on, but these equivalents are held to the atoms by varying attractive forces. A compound which is electrically neutral will have each equivalent of positive electricity neutralised by an equivalent of negative electricity on another atom.

'I think' says Helmholtz 'the facts leave no doubt that the 'very mightiest among the chemical forces are of electric 'origin. The atoms cling to their electric charges, and opposite electric charges cling to each other, but I do not 'suppose that other molecular forces are excluded, working 'directly from atom to atom' (*loc. cit.* pp. 302—303).

<sup>1</sup> Compare also Davy's view, as quoted in book 1. chap. 11. par. 46.

251. Helmholtz thus presents us with a theory of chemical affinity in many respects resembling that held by Berzelius. We are taught to look on each atom as carrying with it a definite quantity of positive or negative electricity; but in place of the varying 'intensity of polarity,' which Berzelius regarded as closely associated, if not identical, with chemical affinity, we have the varying attractive force with which the equivalents of electricity are held by different atoms<sup>1</sup>.

252. The theory of chemical equilibrium propounded by Pfaundler, on the lines of that of Williamson, is quite in keeping with the electrical theory developed by Helmholtz, inasmuch as no work need be done in a chemically homogeneous system in which mutual exchange of similar atoms with similar electrical charges is occurring between the molecules which constitute the system<sup>2</sup>.

253. I have attempted, in the preceding paragraphs of this section to sketch the present state of knowledge regarding affinity, and at the same time to indicate the methods, and the steps, by which this knowledge has been gained.

In the theory of Guldberg and Waage, we are presented with a general statement of the influence exerted by the relative masses of the substances forming a chemically active system on the equilibrium attained by the system, when all the constituents are free mutually to act and react. The total chemical change, in such a case, is the sum of many changes, each of which may be regarded as determined by the resultant of the actions of various forces, both chemical and physical. Eliminating, as far as possible, the physical actions, Guldberg and Waage call the resultant of the actions of the chemical forces, concerned in each part of the total change, the coefficient of affinity for that reaction. The equilibrium of the entire system is determined by the various coefficients of affinity, and by the active masses of all the constituents. If chemical operations are chosen for study which consist, as far as possible, of one primary and one reverse change, values may be found for various coefficients of affinity in terms of some one chosen as unity.

<sup>1</sup> Compare book I. chap. II. par. 47.

<sup>2</sup> See Arrhenius, *Ber.* 17. 49.

But these coefficients of affinity may be further analysed. Ostwald has shewn us how to set about this, in the case of the reactions between acids and bases. When two acids and a single base react, the coefficient of affinity for the reaction may, according to Ostwald, be divided into two parts, one depending only on the nature of the base and the other only on the nature of each acid. In other words, each acid, and each base, exerts a specific influence on the course of the reaction and on the final equilibrium attained by the system. By pursuing this method of enquiry, Ostwald arrives at certain numbers which represent the relative affinities of the acids in terms of that of hydrochloric acid taken as 100. The subsequent researches of this naturalist, we found, on the whole confirmed the values he had assigned to the relative affinities of the acids.

But, as we saw in par. 202, measurements of the changes of energy which accompany changes in the distribution of the chemically different kinds of matter of a system, must throw light on the actions of the forces which come into play in these changes. Such measurements of changes of energy are best accomplished by means of the calorimeter. We found that the thermochemical researches of Thomsen on the phenomena which occur when two acids and one base mutually react, lead, practically, to the same conclusions regarding the relative affinities of acids, as those gained by Ostwald by different methods of investigation.

But the energy-changes which accompany chemical reactions are regarded by the molecular theory as essentially connected with changes in the arrangements of the atoms of the elements which form the reacting systems. Hence, what is desired, is, if possible, to measure the energy-changes which occur along with definite actions and reactions between atoms. Now, we found that thermochemical measurements really represent the sums of many operations, some of which involve evolution of heat, and some, absorption of heat; some of which again are physical and some chemical.

If the term affinity is to be applied only to the transactions between atoms, when viewed from the side of one kind



of the reacting atoms, then thermal methods of investigation cannot at present help us much to a knowledge of affinity. I think it must have been noticed that the term affinity appeared to be continually changing its meaning in the paragraphs wherein the bearings of thermochemical data on this subject were considered. Sometimes affinity appeared to be only another term for chemical change, sometimes it was the force exerted by one atom on another, sometimes it was the energy-change accompanying a change in the arrangement of various chemical substances. When we came to glance at the electrical aspects of the subject, then affinity appeared as nearly if not quite identical with electrical forces. The investigations of Helmholtz seemed to shew us the atoms of every element carrying with them, in their movements, definite charges of electricity, but holding these charges with a force which varies for the atom of each element. Chemical changes appeared to be very largely conditioned by the magnitudes of these electrical charges, and by the forces wherewith the charges are held to the different atoms.

If, in the light of these investigations, the term affinity is still to be employed, it must, at present, have a meaning somewhat vague, or at least wide. When we say that, under given conditions, this compound is produced rather than that, or more of this is produced than of that, because of the differences between the affinities of the reacting elements, we mean, that the final arrangement of the reacting elements is conditioned by the mutual actions of their atoms, and that these actions are largely determined by the electrical charges, and electrical conditions, of those atoms.

Whether the term affinity should be employed at all, with such a meaning as this, is open to doubt.

As long as we deal with certain numbers representing the relative affinities of definite substances, we are on firm ground; these numbers summarise a great deal of information about the substances themselves. But when we attempt to frame a general theory of affinity, we are practically endeavouring to construct a general theory of chemical action, and it is very questionable whether the former, apparently

narrower and more definite term, should not be abandoned in favour of the latter, or some other similar expression. The study of affinity would then be advanced by all the methods which are available for studying the general conditions of chemical equilibrium. These methods, as we found in pars. 185 *et seq.*, are broadly divisible into two groups, thermodynamical and molecular.

Researches such as those of Horstmann, and Gibbs, must largely advance our knowledge of affinity, considered from the thermodynamical point of view, while such investigations as those of Wright, and Helmholtz, must do much to elucidate this subject when regarded from the molecular stand-point.

The theory of Guldberg and Waage, and its development and application by Ostwald, will remain, as the great advance made in recent times in what may be called the practical aspects of the subject of affinity.

## CHAPTER IV.

### OTHER APPLICATIONS OF KINETICAL METHODS.

254. I HAVE frequently referred to the need of keeping distinct the consideration of molecular phenomena occurring in gases, from that of analogous phenomena occurring in solid or liquid substances. Even in the former cases, many occurrences are more probably to be regarded as connected with the actions and reactions of groups, or aggregates, of molecules, than with mutual actions between the individual molecules themselves.

A full consideration of this subject would lead us into the domain of pure physics; there are however some points which suggest important chemical questions.

In examining the phenomena of isomerism, we found that the formula chosen to represent this or that compound, is sometimes selected from among several possible formulæ, by considering certain physical constants of the compound when in the liquid (or even solid) state. In such a case the assumption is made, that some of the physical properties of the compound in question are connected with the relative arrangement of the atoms in the molecule of this compound. The fact that the compound can be gasified and again condensed without any change of properties renders this assumption very probable. In any case, however, the term molecule, as here employed, means, 'that small part of the gas', obtained by heating the liquid compound, 'the parts of which do not part company during the motion of agitation of that gas.' But there are other physical properties which are more usually regarded as depending on the nature of those

groups of molecules, the parts of which do not part company during such processes as diffusion, rise of temperature not involving change of state from liquid to gas, &c. Or, it may be, that the same physical property, e.g. power of rotating the plane of polarisation of a ray of light, is sometimes to be associated with the structure of the *molecules* of a compound, and in other cases with the nature of the molecular aggregates which probably form the reacting units of the same compound when in the liquid state.

The molecular weights and the chemical properties of certain gaseous compounds may be known, and the chemical properties of the liquids obtained by condensing these gases may also be known, and yet it may not be possible to say how far the latter properties are to be regarded as correlated with the mutual relations of the atoms constituting the gaseous molecules of the compounds in question, rather than with the mutual relations of the molecules which probably compose the reacting units of the same compounds when in the liquid state. In other words, it is often difficult to decide whether a definite chemically homogeneous gas is, or is not, to be regarded as chemically identical with the compound obtained by condensing that gas to the liquid form.

The existence of the gases  $S_8$  and  $S_2$ ,  $O_3$  and  $O_2$ ,  $N_2O_4$  and  $NO_2$ ,  $Sn_2Cl_4$  and  $SnCl_2$ ,  $Fe_2Cl_4$  and  $FeCl_2$ , &c., warns us against asserting that all the chemical properties of a gas,—that is, on the present view, the properties dependent on the mutual relations between the atoms which form the molecules of the gas,—are the same as the chemical properties of the liquid which is obtained by condensing that gas.

All precise conclusions regarding the valencies of atoms and the distributions of atomic interactions (so far as such conclusions can be precise) must be applied only to gaseous compounds. Nevertheless, as the chemical relations between compounds are more frequently determined from the study of liquid, than of gaseous substances, we are obliged, granting the theory of valency, to regard these relations as to a great extent conditioned by those between the atoms which constitute the true molecules of the compounds in question. When

however we do not know the molecular weights of compounds in the state of gas, conclusions regarding the structure of the molecules of these compounds are very apt to degenerate into mere exercises of fancy. Indeed the use of the expression 'structure of molecules' is in such cases quite unwarranted<sup>1</sup>.

More than one compound may be produced by the grouping together in various ways of the same molecules, or by variations in the numbers of the molecules which form the reacting unit of each compound. If certain compounds are capable of existing as gases, and if it is assumed that the relative weights of the true molecules of these compounds are known, still it does not follow that the properties of the reacting units of the actually occurring compounds are the sums of the properties of the molecules which form these units. As the properties of a molecule are not the sum of the properties which characterise the separated atoms of that molecule, so the properties of an aggregate of molecules may not be the sum of the properties of the separated molecules; but

<sup>1</sup> Could there be a rough classification of chemical compounds founded on these considerations?

- (1) Compounds, the properties of which are not quite the mean of those of their constituents, but which are easily separated into definite constituents; e.g. sulphuryl dibromide. The gases evolved by heating such compounds are only mixtures, the compounds are not re-formed on cooling these gases; under special conditions, chiefly of temperature and pressure, the gases do combine, but the combinations are very unstable.
- (2) Compounds which can be obtained pure only with much difficulty, if at all; because their properties are connected with the existence of groups of molecules (or groups of atomic aggregates), the composition of which groups varies within certain limits. As soon as attempts are made to remove 'impurities,' these groups become unstable and undergo rearrangement. The vapourisation of such compounds will shew distinct analogies with the process of dissociation, but the gas obtained will probably consist of one kind of molecules only. The terpenes,  $C_nH_{2n-4}$ , may possibly belong to this group of compounds.
- (3) Compounds which dissociate on being heated; the gas evolved from one of these compounds is a mixture of atomic aggregates, which recombine on cooling, to produce the original compound.
- (4) Compounds which do not dissociate, but remain unchanged, when in the gaseous state, to a comparatively high temperature whereat true decomposition begins.

as the composition of such an aggregate easily undergoes change, so do the properties of the compound built up of the aggregates exhibit variations<sup>1</sup>.

No kinetic theory of liquids and solids has as yet been formed, although parts of such a theory may have been sketched in outline<sup>2</sup>.

One point seems clear, namely, that the explanation of the physical properties of solids and liquids, in terms of any molecular theory, demands the existence of groups of molecules, which behave, under certain conditions, as individual systems, but separate into parts more readily than the molecules of gases.

This view is developed in Clerk Maxwell's article on the *Constitution of Bodies*<sup>3</sup>, where a solid is regarded as a body consisting of groups of molecules, 'some of which are in different circumstances from others.' Certain of these groups may break up by the effect of the accumulation of the ordinary agitation of the molecules, while others remain unchanged 'unless the average strain exceeds a certain limit.' The latter, comparatively stable groups, may be disseminated so abundantly through the solid as to form a kind of framework, and thus the solid as a whole 'will not be permanently deformed except by a stress greater than a certain given stress.'

Now chemical phenomena point to the same general conclusion as that obtained by physical methods of enquiry.

255. If then it is so difficult, or even impossible, to apply the molecular theory, in its kinetical aspects, to the chemical study of liquids and solids, it may be necessary to seek for some other guide in this study.

It would obviously be absurd to have recourse to the conception of equivalents apart from the light thrown thereon by the theory of atoms and molecules. Perhaps the best guide in the present state of advance is the periodic law.

We are again brought face to face with the quest so

<sup>1</sup> See Lehmann's classification of physical isomerides, *ante*, book 1. chap. 11. par. 94.

<sup>2</sup> See Sir W. Thomson, *Nature*, 30. 417.

<sup>3</sup> *Encyclopædia Britannica* (9th ed.).

eagerly followed by Dalton and Berzelius, the quest for the laws of atomic synthesis.

Is it possible to generalise the facts regarding the combinations of atoms so as to be able to deduce limiting forms for the compounds produced by the union of any given elements? We saw in a former chapter<sup>1</sup> that such limiting forms may be found to a certain extent, without employing structural formulæ, or indeed committing ourselves to any theory as to the connection between the properties of compounds and the arrangements of the particles which compose them.

The symbols which express the forms of the highest oxides, or other salts, characteristic of any group of elements, do not profess to do more than shew the ratio of the numbers of the atoms of the elements in the reacting units, not necessarily in the molecule, of the oxide or other salt. When the limiting forms have been established, it may perhaps be possible to shew that the running down of chemical energy to the form of heat, which occurs in the combinations of elements, is connected with the forms of the salts so produced; and thus to establish a relation between the limiting forms of salts, and the limits within which the energies of the systems which produce these salts can undergo degradation.

256. Before a structural formula can be assigned to a gaseous compound, or to a liquid the molecular weight of the gas obtained by heating which is known, it is necessary, as we have seen again and again, carefully to study the reactions of the compound in question. The formula finally given to the compound interprets the results of this study in terms of a special theory of the structure of matter.

Now, the interpretation of a number of chemical changes, looked at from the point of view of one of the changing substances, is a problem essentially belonging to chemical kinetics. But our ordinary structural formulæ are for the most part founded on statical considerations, and are too often the products of statical methods of enquiry. The theory of chemical equilibrium sketched in chapter II. of this book (par. 187) associates the nature of a process of chemical change which any

<sup>1</sup> Book I. chap. III. par. 114.

compound can undergo with the affinities of the constituents of the changing system, and with the conditions of motion of these constituents. But the conditions of motion of any substance depend, not only on the motions of the molecules as wholes, but also on that of the atoms, or groups of atoms, which form these molecules, and on the ratio of these two quantities.

Moreover this ratio may, and very probably does vary considerably, in the individual molecules of any one constituent of the system. But any structural formula assigned to a given compound represents all the molecules of that compound as absolutely identical at any moment, and it considers these molecules quite apart from those others by a study of the mutual actions between which and the given compound the formula professes to have been gained.

From a consideration of the work of Willard Gibbs on chemical equilibrium (see par. 193 of this book), taken along with Pfaundler's hypothesis, it follows (as has been pointed out on p. 395), that chemically heterogeneous systems apparently not undergoing chemical change, may be in one of those phases of relative instability which are easily overthrown by contact with small quantities of matter in other phases. This suggests that structural formulæ may sometimes represent the structure of molecules only when they are in certain phases, which are stable in the presence of matter in some other, relatively more stable, phase; or that the phase chosen for representation in the formula may be one which is very easily overthrown by small changes in the surroundings of the compound formulated<sup>1</sup>.

The possibility of one compound passing through several phases, each of which should be represented by a different formula, is, it is true, dimly recognised in some chemical treatises; but the importance of this almost neglected aspect of formula-making is brought prominently forward by the study of chemical change and chemical equilibrium.

<sup>1</sup> The examples given in book I. chap. II. par. 77, will serve to illustrate this suggestion. See also the account of the reactions of the alcohols  $C_4H_9.OH$  in Armstrong and Groves, *loc. cit.* 438—444.



It would be very difficult, perhaps impossible, to include much information regarding the methods of formation, the relative stabilities under different conditions, and generally the 'power of doing' of a compound, in a single intelligible and not too cumbrous formula. I call the student's attention to the kinetical aspects of the structural formulæ now used in chemistry, because I consider it of paramount importance that he should remember how little information these formulæ give in comparison with what we would desire to have, that he should not forget that the experimental methods by which these formulæ are obtained are for the most part kinetical methods, while the interpretation of the results is expressed in a language which has grown out of almost purely statical considerations, and that while he recognises the vast importance of structural formulæ, he may still refuse to bow the knee to this chemical Baal, which has been set up in these times, so aptly described by Remsen as the era of 'formula worship.'

257. Is it possible to connect the structure of the molecules of various compounds, as this structure is expressed in formulæ based for the most part on statical considerations, with the relative affinities of these compounds, which, as we have seen, are numbers obtained by the employment of kinetical methods of research, and which tell a great deal as to the power of doing of the compounds?

The numbers given in the table in par. 235 (chap. III.) represent the relative affinities of a series of acids, including several carbon acids the structural formulæ of which have been well established. If the relative affinities of the chlor-acetic acids are compared with that of acetic acid, and if lactic and trichlorolactic acids are also compared, we have this result.

<i>Acid.</i>		<i>Relative affinity.</i>
Acetic	$\text{CH}_3 - \text{CO}_2\text{H}$	6.3
Monochloracetic	$\text{CH}_2\text{Cl} - \text{CO}_2\text{H}$	22
Dichloracetic	$\text{CHCl}_2 - \text{CO}_2\text{H}$	52
Trichloracetic	$\text{CCl}_3 - \text{CO}_2\text{H}$	87
<hr/>		
Lactic	$\text{CH}_3 - \text{CHOH} - \text{CO}_2\text{H}$	10.5
Trichlorolactic	$\text{CCl}_3 - \text{CHOH} - \text{CO}_2\text{H}$	26

Substitution of Cl for H in acids therefore appears to be attended by an increase in the values of the affinity-constants of the acids.

The substitution of OH for H acts in a similar way. Thus,

<i>Acid.</i>		<i>Relative affinity.</i>
Isobutyric	$(C_3H_7)_2 \cdot CO_2H$	5.8
Hydroxyisobutyric	$(C_3H_6 \cdot OH)_2 \cdot CO_2H$	10
Succinic	$C_2H_4(CO_2H)_2$	7
Malic	$C_2H_3(OH)(CO_2H)_2$	11
Tartaric	$C_2H_2(OH)_2(CO_2H)_2$	15

On the other hand, the substitution of  $CH_3$  for H is accompanied by a decrease in the values of the affinity-constants of the acids examined. This is shewn by the following among other numbers.

<i>Acid.</i>		<i>Relative affinity.</i>
Formic	$H \cdot CO_2H$	12
Acetic	$CH_3 \cdot CO_2H$	6.3
Propionic	$CH_3 \cdot CH_2 \cdot CO_2H$	5.5

But the relative affinities of methyl-, ethyl-, propyl-, and amyl-sulphuric acids, viz. 100.4, 99.5, 99, and 98, shew that the substitution of  $CH_3$  for H in the molecule  $SO_3 \cdot OH \cdot OC_nH_{2n+1}$ , is attended by only a very small decrease of affinity.

Ostwald's numbers further suggest that the values of the affinity-constants of the carbon acids are conditioned by the relative arrangements of the atoms in the molecules of these acids. Thus, comparing the relative affinities of acetic and trichloroacetic acids, with those of lactic and trichlorolactic acids, we see that the difference between the values of the quantities in question is much larger in the case of the former than of the latter pair of acids. Thus,

<i>Acid.</i>		<i>Relative affinity.</i>	<i>Difference.</i>
Acetic	$CH_3 \cdot CO_2H$	6.3	80.7
Trichloroacetic	$CCl_3 \cdot CO_2H$	87	
Lactic	$CH_3 \cdot CHOH \cdot CO_2H$	10.5	15.5
Trichlorolactic	$CCl_3 \cdot CHOH \cdot CO_2H$	26	

The replacement of  $H_3$  by  $Cl_3$  is accompanied by a much greater increase of affinity when there is direct mutual action between the  $Cl_3$  group and the acid group  $CO_2H$ , than when the two groups are separated by the group  $CHOH$ .

The influence of the distribution of the interatomic actions on the affinity-constants of acids is also illustrated by the following numbers.

	<i>Acid.</i>	<i>Relative affinity.</i>
Oxalic	$HO_2C-CO_2H$	43
Malonic	$HO_2C-\overset{H_3}{C}-CO_2H$	17.5
Succinic	$HO_2C-\overset{H_3}{C}-\overset{H_3}{C}-CO_2H$	7
<hr/>		
Lactic	$CH_3-CHOH-CO_2H$	10.5
Methoxyacetic	$CH_3-OCH_3-CO_2H$	13.5

In the three acids oxalic, malonic, and succinic, we notice a rapid decrease in the value of the affinity as the mutual actions of the carboxyl groups become more indirect; and the comparison of lactic and methoxyacetic acids suggests that the presence of the group  $H_3C-OCH_3$  is attended with a greater affinity-value than that of the isomeric group  $H_3C-CHOH$ <sup>1</sup>.

258. One of the general conclusions regarding the relations between the structure of carbon compounds, and the refraction-equivalents on the one hand, and the 'specific volumes,' ( $V$ ), on the other, of these compounds, may here be recalled (see book I. chap. IV. pars. 141, 143, and 154). The refraction-equivalent, and also the value of ( $V$ ), of an unsaturated compound, i.e. a compound in the molecule of which some of the polyvalent atoms act on less than their maximum number of monovalent atoms (see book I. chap. II. par. 62), are always less than the values of the same constants for an analogous saturated compound.

Now Brühl<sup>2</sup> has tried to shew that an increase of the refraction-equivalent is connected with a loosening of the attractions

<sup>1</sup> For more details see Ostwald, *J. für prakt. Chemie*, (2), 18. 362: 28. 479, 488, 492: 29. 403.

<sup>2</sup> *Ber.* 14. 2533.

between the atoms in the molecules of compounds. Brühl's reasoning seems to me to be very unsatisfactory<sup>1</sup>. But a similar conclusion has been arrived at by Schiff from his measurements of the values of (*V*) for a large series of compounds, and from some general considerations drawn from the kinetic theory of gases<sup>2</sup>. Schiff's comparison of (*V*) for the normal acids

$C_nH_{2n+1}C\begin{smallmatrix} O \\ \diagup \\ OH \end{smallmatrix}$  with (*V*) for the normal alcohols  $C_nH_{2n+1}C\begin{smallmatrix} H_2 \\ \diagup \\ OH \end{smallmatrix}$ ,

shews that the value of (*V*) for the monovalent oxygen atom in the molecules of the acids increases as the series is ascended<sup>3</sup>. But, if we admit the general conclusion arrived at by Brühl, and also by Schiff, this increase is accompanied by an increased loosening (*Lockerung*) of the group CO.OH. Such a loosening would, we should expect, be attended by a decrease in the *acidity* of the acids of the series. This conclusion is in keeping with Ostwald's values for the relative affinities of the three acids, formic, acetic, and propionic, viz. 12, 6.3, and 5.5.

Whether Schiff's conclusion is accepted or not must depend upon the results of further investigations. There is one point especially worthy of note in the nature of the argument adopted by Schiff, namely, it is based on measurements of the changes in the values of (*V*) which accompany definite chemical operations. This, it seems to me, is as it should be. As we require determinations of the changes of energy which accompany this or that chemical change, so we must have determinations of the variations in such physical constants as (*V*), (*R<sub>A</sub>*), &c., which proceed along with definite, and if possible simple, chemical processes.

There appears to be a definite connection between the course of a chemical operation and the ratio of the original to the final volume of the reacting system. W. Müller-Erbach has endeavoured to express this relation in the so-called 'law of smallest volumes,' which states, that the smaller the volume occupied by the products of a chemical change, the greater

<sup>1</sup> In connection with this see Thomsen, *Ber.* 15. 67.

<sup>2</sup> *Annalen*, 200. 321.

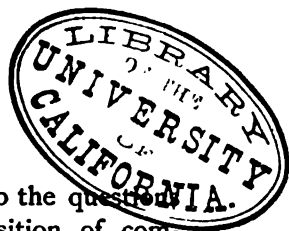
<sup>3</sup> For data see Schiff, *loc. cit.* 314—315.

is the loss of energy during the change, and therefore the more probably will the change occur<sup>1</sup>.

259.- Ostwald's researches suffice, I think, to establish the existence of a connection between the structures and the affinities of molecules. In other words, these researches put an instrument into the hands of chemists by the use of which they may hope to gain a more complete answer than has hitherto been possible to some of the questions which lie at the root of chemical science. A structural formula, which is the result of an extended investigation, summarises a great many facts about the composition, and also tells something of the reactions, of the compound formulated; the number which represents the relative affinity of the same compound is obtained by comparing the power of doing of the substance with that of other substances, and enables us, to some extent, to predict the course and the results of the chemical changes that will occur in given systems of which the substance forms a member.

The structural formula is based on the molecular and atomic theory, and, in so far as it has been obtained by assuming the theory of valency, it includes in its expression the older views regarding equivalency. It may be possible, some day, to indicate by this formula the relative loss or gain of energy which has occurred in the passage from some standard state to the state expressed by the formula. The relative affinity, on the other hand, is based on a kinetic theory of chemical action, and is the outcome of the study, for three-quarters of a century, of chemical change. We begin to see how the formula and the affinity may be merged into a common expression, which shall tell us, not only the composition, but also the function of the substance, and in doing so will reconcile the two schools which have so long existed in chemistry, the school of Bergmann, Berzelius, and Dalton, with that of Berthollet, Davy, and Dumas.

<sup>1</sup> *Annalen*, 218. 113. See also *Ber.* 14. 217 and 2212; 16. 758; 17. 198. Also Donath and Mayrhofer, *Ber.* 16. 1588. Compare also Spring's work on the connection between allotropy and volume; see foot-note on p. 137.

*Concluding Remarks.*

We have thus tried to gain some answers to the questions with which we started, What is the composition of compounds? What actions are compounds capable of performing? A complete answer to either question will be an answer to both, and that answer will include the whole of chemistry.

The atom of the chemical element has been the unit with which we have had to deal; the properties of compounds have been regarded as conditioned on the one hand by the nature, the number, and the arrangement of the elementary atoms which together form the compound molecules, and on the other hand, by the greater or smaller quantities of energy associated with these molecules. To determine the relations between the properties of various molecules, and the nature, number, and arrangement of their constituent atoms was the first part of our task; to attempt an outline of a dynamical explanation of chemical operations between molecules was the object of the second part of the undertaking.

But inasmuch as the properties which chiefly concern us as chemists, are the properties, not of individual substances, but rather of these considered as members of changing systems, it has been impossible to consider the questions arising in the first part without to a great extent making use of methods, and conceptions, more strictly belonging to the second part of our subject.

The facts connoted by the expression chemical statics were to some extent classified by the help of the hypothesis of valency, itself an outcome of the application of the molecular and atomic theory to chemical phenomena, and by the hypothesis regarding the relations between the atomic weights of the elements, and the properties of these elements and their compounds, which is known as the periodic law. The determination of physical constants, and more particularly the

quantities of heat evolved or absorbed during chemical changes, the refraction-equivalents and specific rotatory powers, and the relative volumes, of typical compounds and classes of compounds, helped somewhat towards a definite knowledge of the composition of these compounds.

The study of chemical kinetics was, we found, much advanced by the dynamical hypothesis of Guldberg and Waage, which in its primary form is nearly independent of any molecular theory of the structure of matter, but in its development and application by Ostwald forms a bridge connecting the investigation of the chemical properties of molecules with that of the actions of the forces which come into play during chemical operations. The thermodynamical methods of investigation introduced by Horstmann, Gibbs and others, and the electrical methods founded on the work of Joule and Thomson, and developed by Helmholtz and Wright, also helped us to gain some conceptions of the conditions under which chemical changes proceed, and chemical equilibrium is established, and at the same time threw a little light on the most profound parts of chemical phenomena, the nature and conditions of action of the forces concerned in the combinations and decompositions of the elementary atoms.

I have tried always to exhibit the hypotheses of chemistry as at once arising from facts, and serving as guides in the quest for facts. It is especially necessary to do this, I think, in dealing with the questions concerning structural formulæ. If these formulæ are dissociated from the chemical facts which they symbolise they become intellectual tyrants; if each formula is considered simply as a summary of facts regarding the compound formulated, they are to be classed with the other 'brute beasts of the intellectual domain,' and cease to have much interest for one who believes that chemistry is a branch of science.

One great difficulty in using chemical hypotheses consists in determining the limits of the class of phenomena to which each hypothesis may be applied. Berzelius carried the hypothesis of dualism too far, and it was destroyed by the more elastic hypothesis of substitution; in our own day the hypo-

thesis of valency has frequently been applied to phenomena with which it has little or nothing to do.

But each failure to explain all in terms of one hypothesis makes us more hopeful for the future, and convinces us that we have to deal with a living and growing part of the study of nature.

Much work has yet to be done before a general theory of chemical change can be hoped for; a theory which shall represent every process of change as a function of the atomic weights of the elements, and the affinities of the reacting substances concerned in the operation. When such a theory is attained, will chemistry be complete? I hope not; for

‘What’s come to perfection perishes.’





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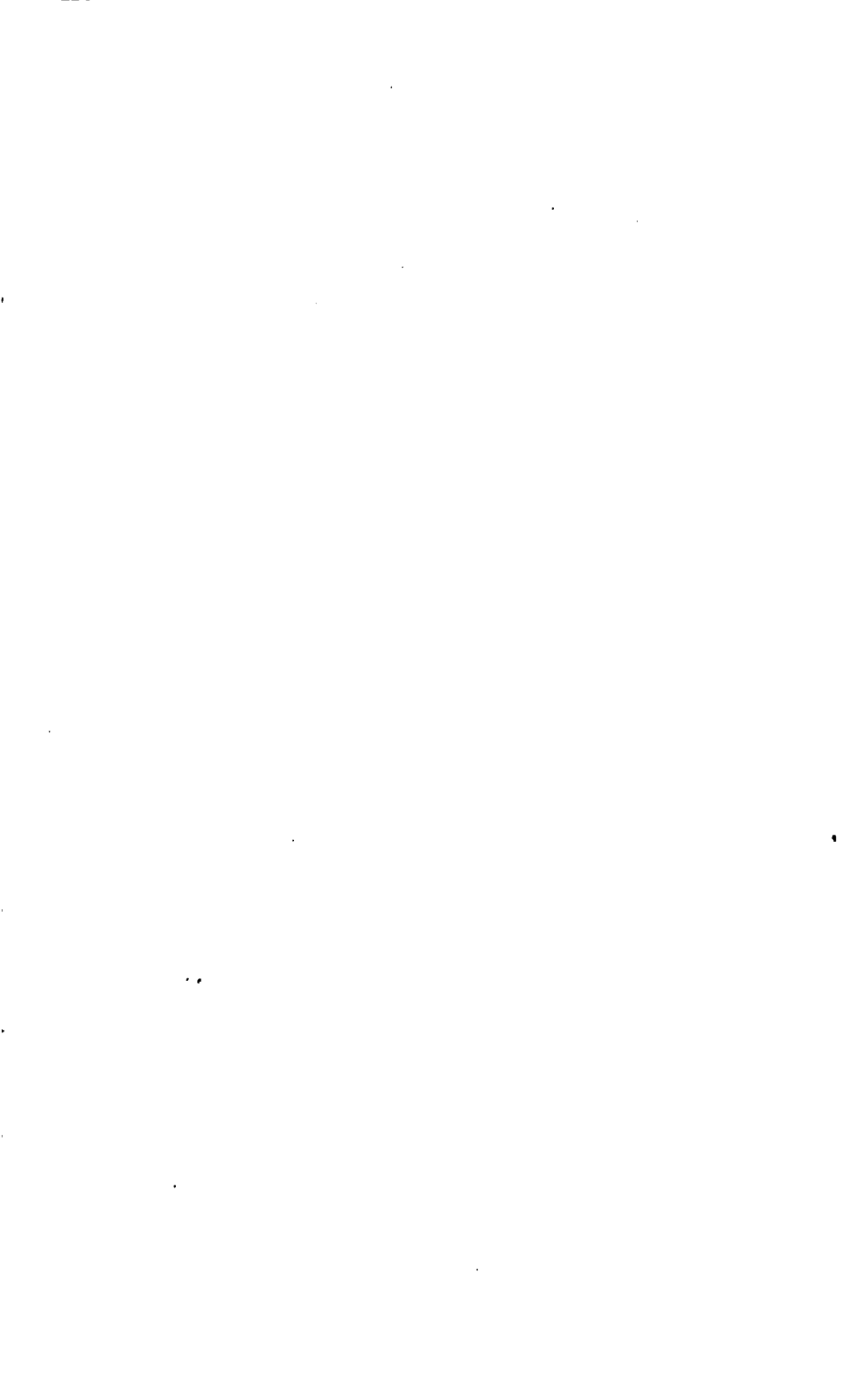
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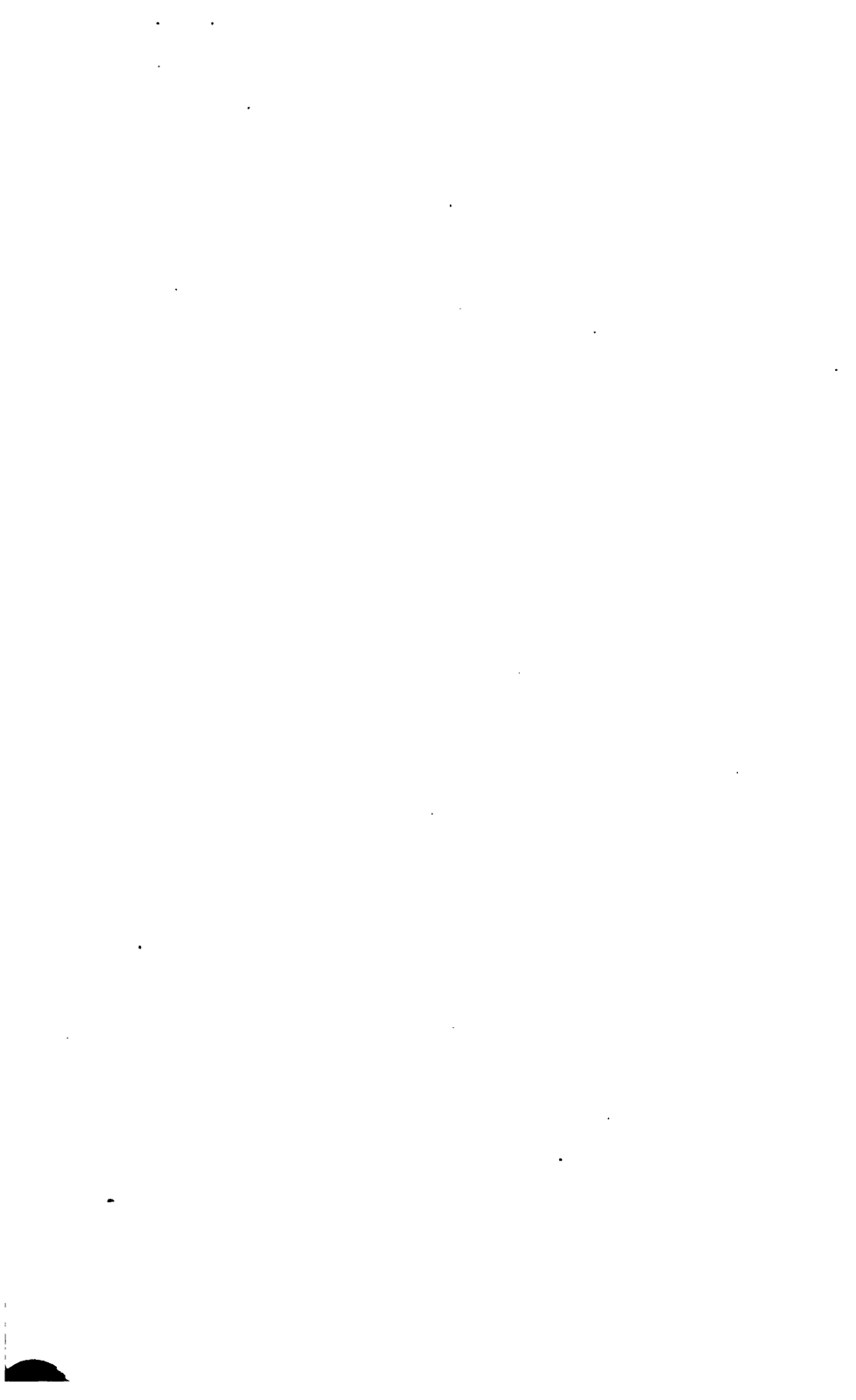
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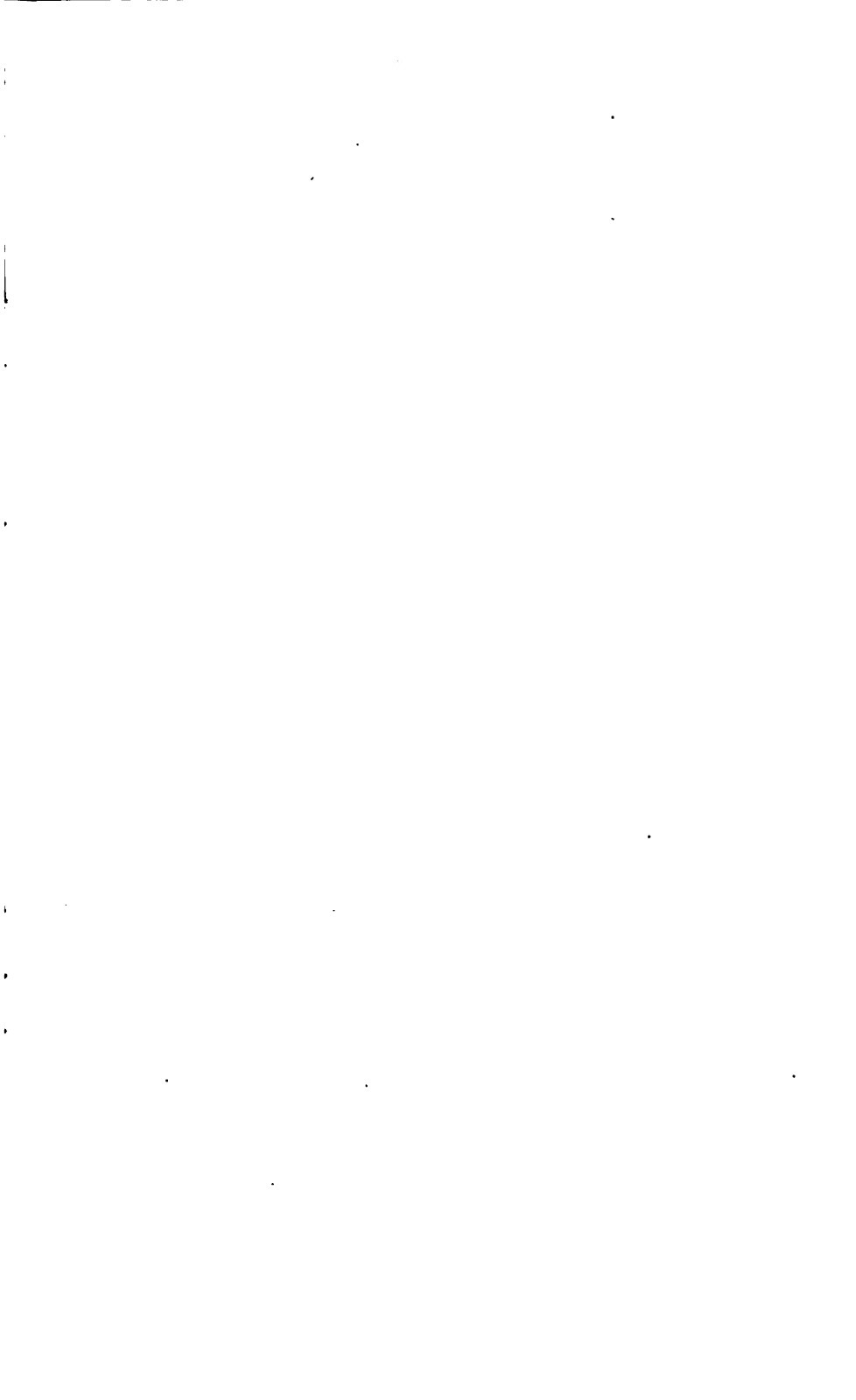
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